MODERN PLASTICS

By the Same Author

MODERN RUBBER CHEMISTRY

MODERN SYNTHETIC RUBBERS

MODERN PLASTICS

By

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TO

MY MOTHER

FOR HER SACRIFICE AND FORETHOUGHT

AND

MY WIFE

FOR HER PATIENCE AND INSPIRATION

PREFACE TO SECOND EDITION

A REASONABLE time has now elapsed since the end of the war to form a balanced view of the plastics industry. There has been a complete change over from a war economy to a peace economy. The enormous expansion of the plastics industry brought about by war conditions has not only been maintained but has been left far behind. The plastics industry has now attained the status of a major industry. The innumerable new outlets which have appeared for plastics have created a tremendous upsurge in demands. These have been so great that considerable strain has been imposed on sources of raw materials. Shortages have appeared in every direction, notably in the case of plasticisers. The supply of coal products has been inadequate. In many cases coal is the only source of supply and the shortages have created great difficulties. A consequence has been the rise of chemical industries based on other materials, notably petroleum.

As anticipated there have been phenomenal developments in some fields of plastic application. Polyvinyl chloride and polystyrene have been outstanding, particularly in the United States. The development of polystyrene can be directly attributed to the U.S. synthetic rubber industry. In Great Britain where sources of raw materials have been very limited, development has been particularly marked in the use of P.V.C. The use of P.V.C. paste in Great Britain is outstanding.

New fields of activity which have matured during the last few years include the silicone resins and the so-called contact resins. Still in their early stages they seem destined for considerable expansion. On the chemical side there have been some important new developments which may have considerable repercussions on the future pattern of the plastics industry. Reppe chemistry, the chemistry of acetylene, has made great strides, particularly in Germany. Many processes have been developed for obtaining chemicals for petroleum, one of the most outstanding being the Catarole process. All these processes, apart from providing standard plastics, give promise of yielding materials for new types.

In spite of the great difficulties which have been experienced in Great Britain we have been doing very well. The over-all production of plastics compares favourably with the U.S. on a population basis.

There have appeared a large number of reports on German industry, produced by the Combined Intelligence Objectives Sub-Committee, referred to as C.I.O.S., and also by the British Intelligence Objectives Sub-Committee, referred to as B.I.O.S. Whatever their value in other industries those dealing with plastics have been extraordinarily good. Their importance lies not so much in the novelty of the subjects discussed, but in the minute practical detail such as cannot be found in any other publications or patent specifications.

So far as the future of the plastics industry is concerned, its continued prosperity still depends upon the proper uses of the individual materials. Neglect of this cardinal principle creates great resistance amongst the consuming public.

HARRY BARRON

SOUTHAMPTON,

1949

PREFACE TO FIRST EDITION

For some time past there has been a great necessity for a book giving the fundamental background covered by the term "Plastics". The subject has expanded at a rapid rate, especially during recent years. There is a very wide interest, mainly uninformed. The desire for technical information is very strong.

This book is an effort to provide an adequate technical background. It is of the utmost importance to provide an authentic technical background for the many thousands who are interested. It is a national necessity that such a work should be available. I hope that any reader with a modest scientific or engineering knowledge will be able to obtain an over-all view of the industry. He can then follow his own particular bent in the current literature. I cannot hope to satisfy fully any specialist. I have not written the book for the experts.

An endeavour is made to cover an extremely wide range of materials. A knowledge of the fundamental background is essential before venturing into new fields.

It may be objected that I have omitted certain common materials such as shellac, bitumens, rubber plastics, etc. This is a deliberate omission on my part. Since these materials are off the main-stream of current plastic development, their inclusion would have curtailed the treatment of the other materials. Also I have not given any consideration to materials such as allyl resins, silicon resins, boron resins, etc., although I am fully aware of their existence. These materials are just not available in this country: they are still of academic interest. As my main intention is to provide information of practical value I do not consider it worth while at this stage to devote space to these materials. It is time enough to consider these when you know something about phenol-formaldehyde, polyvinyl chloride, etc.

I am fully conscious that each individual plastic requires a book to itself for really adequate treatment. However, the newcomer is much more concerned with the somewhat bare outlines. Inevitably in some respects the presentation must be somewhat sketchy to the erudite. However, while an expert on phenol-formaldehyde resins may find the treatment of his subject somewhat elementary, yet he may find compensation in the discussion of some of the other materials.

Organising the subject-matter is difficult, so I have adopted the scheme based on the association of ideas. Moulding is associated with phenolic resins; injection moulding with cellulose acetate; extrusion with polyvinyl chloride; fibres with nylon; safety glass with polyvinyl butyral; and that is where you will find them.

Plastics education is of the greatest importance to the welfare of this country. The industry may attain major importance. It cannot do so with the present minute number of competent technicians. It is absurd to expect that a major industry can be based on a mere handful of fundamental scientists and a couple of hundred competent technicians. It requires the growing and ever-widening interest of many thousands of technicians of every description contributing their ideas to the general pool. The idea of "back-room boys" applied to plastics would be entirely harmful. Quality is important, but quantity no less so.

It should be recognised that the joint efforts of many thousands, applied to the derivation of raw materials from coal, would rapidly solve many of our plastics raw materials problems. The efforts of a few will take correspondingly longer. Similarly, a more objective consideration of oil-refining in this country would bring many benefits to a number of industries, not the least being the plastics industry. In any event we have a great Empire to draw upon for raw materials.

There has been too much misguided obstruction in the way of providing adequate education facilities in this country. The Institute of the Plastics Industry and the British Plastics Federation have made very noteworthy efforts in this direction, which have, however, been nullified by the unimaginative influence of the Treasury. Mere airy talk about expansion of technical education will not help industry. The talk must be implemented by action—and rapid action at that.

There is a wonderful future for Plastics, and it may become a great national asset, but no industry, no asset, is ever acquired without considerable effort and expense. Plastics is no exception to the rule.

This is quite a lengthy book made up of many words and pictures describing numerous materials. But "an ounce of practice is worth a ton of precept." It is absolutely imperative for the reader to obtain these materials, to examine them, handle them, smell them, and so on. That is the only way in which to get any real idea of the subject.

I have had excellent opportunity of trying out the subject-matter incorporated in the book in the form of lectures delivered at University College, Southampton, to very mixed groups of students. I am encouraged to believe that a much wider circle may benefit from them. I have also had the inestimable advantage of having handled in really large quantities most of the materials I have written about.

This has been written in Southampton on the eve of the Allied invasion of Europe. I cannot conceive of any single event which could bring home more strongly the present significance of plastics. From my window I have seen the massive panoply of war, weapons, materials, etc., incorporating vast quantities of plastics in every shape and form, pass on the way to action. I look forward to the corresponding applications in more peaceful activities.

Years ago I suggested in a number of articles that there was no longer any sharp division between rubber, synthetic rubbers, and plastics. This book concludes my work on this theme, completing a trilogy, having been preceded by *Modern Rubber Chemistry* and *Modern Synthetic Rubbers.* In the meantime the whole subject has crystallised as the new science of High Polymers.

My endeavour has been to make clear the technical perspective on this subject.

My own desire is to see Britain leading in these activities and not trailing behind. Lack of knowledge and lack of effort results in the facile and disastrous industrial policy of purchasing foreign licences for processes and goods. This is the easy way out. But it subsidises foreign development and effectively stifles our own. We can no longer afford such luxuries. There never was a more apt quotation than "He who follows must always be behind."

In conclusion, there are two points which must be stressed strongly. The first is that plastics should only be used for purposes for which they are suited. The materials do many jobs well, but they cannot do every job. Choose the right material for the right job. Neglect of this principle tends to give plastics a bad name—quite unjustifiably.

The public must be made conscious of the fact that the magic of plastics merely reflects the technical and scientific knowledge behind them. There is already much evidence of unscrupulous schemes to exploit the high reputation of plastics. If people do not check upon the qualifications and associations behind schemes into which they put their money, then we shall merely have yet another succession of financial scandals.

HARRY BARRON

SOUTHAMPTON,
1944

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PART I

INTRODUCTORY

CHAPTER I

INTRODUCTION

AT the present time there are a number of commercial materials which are described as plastics. Plastics are essentially industrial materials based on synthetic organic chemicals which are not found in nature.

Actually there are more than twenty quite different leading types of materials. The following Table summarises these and gives some additional helpful information. The types refer to the actual plastic materials. These plastics already play a great part in the national economy.

There are two main well-defined classes of plastic materials—thermoplastic and thermosetting plastics.

Thermosetting materials are those which, when subjected to heat (and pressure) become set and infusible. When once cool they can no longer be softened by further heating. They are also insoluble in solvents. The leading examples of thermosetting plastics include phenol-formaldehyde resins, urea-formaldehyde resins, melamine resins, and alkyd resins. They undergo a specific chemical reaction during heating.

Thermoplastic materials are those which become soft and plastic when subjected to heat and pressure, but when cooled again they become rigid. These processes can be repeated indefinitely. There is no chemical reaction during the heating process so that no permanent change occurs. Outstanding examples include cellulose acetate, polystyrene, etc.

Although a very considerable part of plastics activity is concerned with synthetic resins there are other synthetic materials of great importance. For example, the cellulose plastics, casein, shellac, and bitumen cannot by any stretch of definition be regarded as synthetic resins. The subject is rather wider than covers any particular group of synthetic resins.

Properties in common. All plastic materials whether synthetic resins or otherwise, have certain properties in common. The outstanding feature is that they are all thermoplastic at some stage. It is only after a heating process that the diverging properties begin to

TABLE I
THE IMPORTANT PLASTICS

THERMOSETTING PLASTICS	SOME LEADING TYPES
Phenol-Formaldehyde Resins (also known as Phenolic Resins)	Bakelite, Mouldrite, Rockite, Durez, Makalot, Elo, Nestorite, etc.
Phenol-Furfural Resins	Indurite, Durite
Aniline-Formaldehyde Resins	Panilax, Plaskon
Urea-Formaldehyde Resins (also known as Amino-resins)	Beetle, Mouldrite, Scarab
Melamine Resins	Melmac
Alkyd Resins (also known as Glyptals)	Paralac, Beckacite, etc.
THERMOPLASTICS	
Cellulose Plastics—	
Cellulose Nitrate	Celluloid, Xylonite
Cellulose Acetate	Bexoid, Celastoid, Rhodoid, Cellomold, Tenite, etc.
Cellulose Acetobutyrate	Tenite
Ethyl Cellulose	Ethocel, Hercules
Ethenoid Plastics (also known as Vinyl Plastics)—	
Polythylene	Alkathene (polythene), Lupolen
Polystyrene	Distrene, Styron, Laolin, Trolitol
Polyvinyl Alcohol	——
Polyvinyl Chloride	Corvic, Koron, Vinylite QYNA, Geon
Polyvinyl Chloride-Acetate	Vinylite VYNW
Polyvinylidene Chloride	Saran
Polyvinyl Acetal	Alvar
Polyvinyl Formal	Formvar
Polyvinyl Butyral	Saflex
Polyacrylic Esters	——
Polymethacrylic Esters	Perspex, Diakon, Lucite, Plexiglas, Crystallite
Unclassified—	
Polyamide	Nylon, Igemide
Casein	Erinoid, Lactoid, Galalith
Shellac	——
Bitumen	——
Coumarone-Indene	——
Silicone Resins	Silastic
Allyl Resins	C.R.39

This is not a comprehensive list. Most of these names are Registered Trade Marks.

develop. The thermosetting resins such as phenol-formaldehyde resin or urea-formaldehyde resins when heated at first become soft just like all the others. When the heating has been continued for a sufficient period they change to a rigid rock-like product which can no longer be softened. In sharp contrast, the other materials can only harden when cooled, but can thereafter be softened again.

It is this common property of thermoplasticity which is responsible for the development of plastics, for it enables the materials to be used by mass production methods. In the case of setting resins, the change to the rigid condition can be accelerated so as to take place within a few seconds if desired. In practice, what happens is that the resin in the form of a powder is placed in a mould, put into a press, and subjected to heat and pressure. The heat softens the resin and the pressure forces it to take up the shape of the mould. In a few seconds it has become rigid and can then be ejected immediately as a finished reproduction of the mould.

Another feature they have in common is that each type has a large and complex molecular structure. The synthetic resins start from simple chemical entities, most of them quite familiar chemicals. They are then caused to build up to the resinous condition, when they acquire the desirable physical properties. The process in most cases is known as polymerization. In the case of the cellulose plastics the long structure already exists having been built by nature.

Another feature which all plastics have in common is the ability to form strong films either from solutions in solvents or by mechanical processes. This accounts for their prominence in the industries where coatings are involved, e.g. paint, artificial leather, etc.

Plastics is a generic term covering this multitude of materials, each type having a different composition and very different properties. New types are continually being developed. Many thousands have been produced in the laboratories, but only very few possess the necessary combination of properties which justify their large-scale production. It is no exaggeration to say that most laboratories dealing with chemical development have some interest in plastics.

The Difference between Thermoplastics and Thermosetting Resins. The processing properties of the two types differ. The processing of the thermosetting compounds always requires a two-stage operation (the shaping and the setting). There is only one stage in the processing of thermoplastics; there is no danger of premature setting. The processing of thermoplastics is therefore fairly simple and inexpensive, which accounts for their increasing use for numerous applications.

Because thermoplastics are not subject to chemical alteration in processing, any scrap formed during manufacture may be re-used.

The handling of plastics is essentially that of shaping, getting them into some desired form. In order to be processed the plastic material must flow readily under pressure, i.e. it must have a high plasticity at the shaping temperature. In the temperature range in which the material is to be employed it should not flow readily under pressure, i.e. it must have a very low and constant plasticity. The curve showing the plasticity behaviour of desirable materials must therefore be flat in the range of temperatures where the material is in practical use. In particular this should apply to plastic flow under mechanical stresses. It should then take a sudden rapid upward sweep so that the material almost immediately becomes very plastic at a suitable and convenient processing temperature, in fact, almost a melting point. This temperature must, of course, be well below the decomposition temperature.

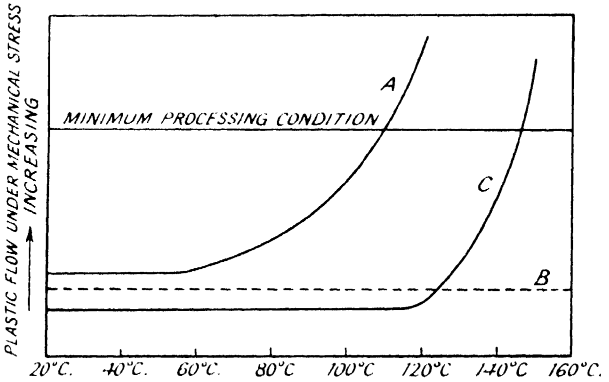


Fig. 1. *A*—Behaviour of typical thermoplastic
B—Behaviour of thermosetting plastic *after* setting
C—Behaviour of desirable type of thermoplastic

This desirable type of behaviour is shown by comparatively few thermoplastic materials. The temperature range in which their properties are indicated by a flat curve is all too short, particularly at the upper temperature. In other words, the top temperature for use is almost invariably lower than is desirable. Three materials, polythene, polyvinylidene chloride, and nylon, show the desired behaviour; that is to say, that their plasticity does not increase appreciably with temperature, but there is a very sudden increase in flow just before the melting point.

With most of the other thermoplastics the plasticity or tendency to flow increases gradually with the temperature, so that the same mechanical pressure has a greater deforming tendency as the temperature increases.

Thermosetting materials such as phenol-formaldehyde resins, urea-formaldahyde resins, etc., undergo a chemical change during or after the shaping process. The plasticity curve which applies during processing prior to the chemical change resembles that applying to thermoplastics. It is completely different from the curve which applies to the product after the chemical change has taken place.

Sources of Plastics. There are many factors that affect the availability of plastics. There is a surprisingly wide range of chemical raw materials used in the manufacture of resins. Some of the most important of these are alcohol, acetic acid, formaldehyde, butyraldehyde, ethylene dichloride, benzol, phenol, cresols, acetone, acetylene, urea, various inorganic acids, cotton linters and wood pulp. This list is again supplemented with many plasticisers which are required for plastics. Often it is the plasticisers rather than the resin components which become the determining factor in the availability of the final plastic. Another controlling factor is the equipment required to manufacture the various items.

TABLE 2

ANNUAL PRODUCTION OF CERTAIN STRUCTURAL AND INDUSTRIAL MATERIALS IN THE UNITED STATES, 1939 AND 1944
(in millions of pounds)

Material	1939	1944
Steel*	105,597	179,283
Copper**	2,279	3,691
Aluminium†‡	427	2,179
Plastics	255	907
Magnesium†§	7	367
Percentage of production of plastics, aluminium, and magnesium to that of steel . . .	0·7	1·9

* Includes ingots and steel for castings.
** Includes primary and secondary production and refined copper imports.
† Includes primary and secondary production.
‡ Includes in 1939 estimated 100,000,000 pounds of secondary aluminium.
§ Includes in 1939 estimated 200,000 pounds of secondary magnesium.

Sources: American Iron and Steel Institute, American Bureau of Metal Statistics, and U.S. Tariff Commission.

Based on figures for 1944, the production of plastic materials approximated 24·6 per cent of that of copper and 41·6 per cent of that of aluminium, and greatly exceeded that of magnesium.

At the present time there is a very great urge for accurate information about plastics. There exists a vague, woolly knowledge which associates plastics entirely with moulded articles. This same section of the public is somewhat bothered because these rigid moulded articles are certainly not plastic. The realisation is gradually dawning that the subject goes much further than this. In one industry after another it has been realised that plastics materials have entered into their particular field of activity and have performed tasks to a standard which could not previously be attained. For example, it has become quite evident that plastics have invaded some of the fields held by wood, metals, glass, ceramics, rubber, and so on.

Yet this angle of substitution can be very greatly over-exaggerated. To bring it back into perspective Table 2 shows how small the entire consumption of plastics is in relation to metals. This takes no cognisance of the enormous amounts of wood, ceramics, glass, etc.

The recent war speeded up the trend for the use of plastics and greatly increased the tempo. In fact, shortages of every description have been made good either partly or in some cases entirely by the use of newer materials. Plastics established themselves as raw materials for the manufacture not only of decorative gadgets and utensils, but for all the paraphernalia of modern war.

One unfortunate result of this general utility is that it has afforded an easy way out for politicians or industrialists in difficulties, to suggest in the vaguest possible terms that some unusual objective may be attained by the use of plastics. Such uninformed optimistic interest, although flattering, does great disservice so far as the welfare of the industry is concerned.

Definition of Plastics. In view of the great potential importance of the plastics industry, there should be a much wider knowledge of plastics. There is a general desire for definitions concerning plastics generally. The term itself is so vague and ambiguous and consequently somewhat misleading. Comparatively few materials show any obvious outward sign of being plastic. After all, the general conception of "plastic" is something soft and yielding. In this respect none of the commercial materials conform. Certainly the products with which most people are accustomed—hard mouldings—in no way convey any impression of plastic character.

Actually the name "plastic" is based on the manipulation of these materials rather than any inherent characteristic. Carleton Ellis[2] has defined the term "plastic" "as being anything which possesses plasticity, that is, anything which can be deformed under mechanical stress without losing its cohesion, and is able to keep the new form given to it."

According to Yarsley and Couzens,[8] "a plastic material is just one which at some stage in its history was capable of flow, and which, on the application of the necessary heat and pressure, can be caused to flow and take up a desired shape. Likewise, a plastic product is one which has been formed under the action of heat and pressure, and which has taken on a permanent shape when these agencies were withdrawn. The plastics industry is the term rather loosely applied which covers the many diverse industries acknowledged in the production of the heterogeneous miscellany of plastic products."

In general, a plastic material is a mixture or combination based on organic compounds or substances, which, under the combined and simultaneous influence of heat and pressure, becomes sufficiently fluid to permit forming to shape. Other materials, such as metals, may, under similar conditions, be in a plastic state, but the term "plastics" is reserved primarily for organic combinations, usually resinous or resin-like condensation, polymerisation, or esterification products. When these are mixed with modifying agents such as plasticisers, fillers, or the like, the resulting product is usually called a plastic material after it is formed to shape. The term "plastic material" is usually reserved for the end product of the process, even though there may only be a plastic intermediate stage.

The American Society for Testing Materials has recently defined the term in the following manner.

Definition of the noun "Plastic." A plastic is any one of a large and varied group of materials which consists of, or contains as an essential ingredient, an organic substance of large molecular weight; and which, while solid in the finished state, at some stage in its manufacture has been or can be formed (cast, calendered, extruded, moulded, etc.) into various shapes by flow—usually through the application singly or together of heat and pressure.

This definition indicates that correct usage for designation of a single material will be "plastic" and not "plastics."

It should be clearly understood that the plastics industry, so far, has only been concerned with organic materials. However, latterly, some success has attended the efforts to introduce inorganic materials into the actual plastic base. In particular, silicon ester resins are beginning to appear. Thus it has been predicted that by 1950 the introduction of partially oxidised silicon into the molecular structure of a new plastic will combine the advantages of organic and inorganic materials. Such "materials of to-morrow" will exhibit enormous strength, rigidity, resistance to weathering, and oxygen. They would be cheaper and lighter than any plastics now used as engineering materials. Silicon resins are already well established as commercial materials and are being manufactured on an ever-increasing scale.

Actually, most plastics are materials which fall into the border area between elastic materials and rigid brittle materials. Thus an elastic product based on rubber can be easily pushed out of shape, but when the stress is released, it goes back to its original shape rapidly. Plastics such as polyvinyl chloride and polyvinyl butyral also have elastic properties. The difference is that when they are stretched, they regain their original dimensions more slowly than in the case of rubber. Brittle materials break readily under mechanical stress. Some types of phenolic resins are clearly nearer the solid brittle type of material, and have little in common with elastic materials.

A Complex Industry. The most spectacular advances in the use of plastics have occurred in the United States and in Germany. We are rapidly catching up in this country.

TABLE 3

UNITED STATES PRODUCTION OF RESINS AND PLASTICS

Year	Synthetic Organic Resins Lb.	Cellulose Plastics Lb.
1927	13,452,000	*
1928	20,411,000	*
1929	33,036,000	*
1930	30,868,000	*
1931	36,179,000	*
1932	30,937,000	*
1933	45,200,000	15,825,000
1934	59,915,000	*
1935	95,133,000	26,695,000
1936	132,913,000	*
1937	163,031,000	37,047,000
1938	130,359,000	*
1939	213,028,000	34,169,000
1940	276,814,000	35,765,000
1941	437,800,000	55,000,000
1942	426,731,000	*
1943	500,000,000	107,000,000
1944	690,000,000	106,000,000
1945	808,000,000	
1946	994,000,000	133,000,000
1947	1,252,000,000	95,000,000

* Figures not available

In some respects this is easily accounted for by the fact that these are the leading chemical producers. For it must be recognised that the plastics industry is chemical by nature. In the United States and in Germany the public have been made acutely conscious of plastics for a number of years.

German consumption of plastics in 1938 was on a very large scale which had expanded considerably by 1944.

The plastics industry is chemical by nature and is closely connected with certain other chemical industries, especially rayon and synthetic rubber. Thus in 1948, in the United States, of the 1,120 million pounds of rayon yarn produced, 375 million pounds were of the cellulose acetate variety, almost identical in composition with the cellulose acetate plastics and sharing their complexities of manufacture and economics.

TABLE 4

BRITISH PLASTICS PRODUCTION

	Tons					
	1941	1942	1943	1944	1945	1946
Cellulose Acetate						
Moulding Powder	1,207	1,343	1,489	1,307	2,162	4,294
Sheets and Tubes, etc.	2,335	2,718	3,059	2,623	1,133	1,443
Cellulose Nitrate	1,719	1,531	1,486	1,572	1,976	2,100
Phenolic Moulding Powders	13,521	13,124	14,289	15,249	17,531	25,221
Urea-Formaldehyde Moulding Powder	4,136	4,080	3,869	2,760	3,996	6,741
Polyvinyl Chloride						
Polymer			745	3,365	4,122	5,471
Compound				10,082	5,463	10,074
Acrylic Resins	1,463	2,507	3,796	4,718	1,832	3,949

Source: Annual Abstract of Statistics

Furthermore, in many of its phases the rapidly budding synthetic rubber industry can hardly be distinguished from the plastics industry. Its Thiokol, Geon, Resistoflex, and numerous other types are really rubber-like plastics, while both industries have in common similar problems of polymerisation, compounding, and processing, in addition to using large quantities of the same raw materials. Butadiene itself, the basic raw material for the chief types of synthetic rubber, notably GRS, has recently been the basis of numerous patents for the production of various new plastics. This 1,000,000-ton-per-year industry is, of course, now shrinking, but, linked as it is with plastics, will serve again to show the important position already attained by plastics in the economic picture.

The United States is by far and away the largest producer and consumer of plastics. It is followed by Germany; Great Britain ranks third amongst the nations in this respect, but every country having any sort of industry has already acquired some interest in plastics.

GERMAN PLASTICS PRODUCTION, 1943[4]

Polyvinyl Chloride	80	million lb.
Polystyrene	16½	,, ,,
Acrylic Plastics	61	,, ,,
Cellulose Acetate	7	,, ,,
Phenolic Resins	70	,, ,,
Urea Resins	75	,, ,,
Polyamides	7	,, ,,

In Great Britain the trend has been appreciably slower. Latterly, following on pressure of war conditions, it has accelerated to an astonishing degree, and at the present time the country is more plastics conscious than ever before. Every industrial country has made strides in the use of various specific types of plastics. It is quite clear that in the U.S.S.R. these materials have been employed on an impressive scale without undue emphasis having been given to these activities. No statistics are available by which one might assess the strength of their industry. There is a large volume of published technical work of high quality. This is generally an indication of an advanced industry.

The Scope of Plastics. Although the electrical industry and the radio industry are the oldest and largest consumers of synthetic resins, plastics have entered many new fields of activity. Not only are they used alone, but they are widely employed in conjunction with other materials as parts of products. As a class of materials they have a number of outstanding attributes. Without exception they have great strength. They can be coloured prior to moulding, and during the moulding not only do they retain these colours but they also acquire an excellent finish. Giving such results by mass production methods they have replaced materials such as wood, glass, rubber, and metals for many applications.

Included among the large industries invaded by plastics are engineering, motor manufacture, aircraft, furniture, domestic appliances, building, chemical industries, packaging, rayon industry, etc. The phenomenal rise of plastics from an insignificant assortment of trades to an industry of great economical and social importance has taken place during the last decade.

It is the strangest fact that in the period of depression, when most industries were in great difficulties, the plastics industry continued to enjoy uninterrupted expansion and prosperity. There is no evidence of recession or standing still. The industry is still in its infancy, and its spread into other industries is so wide and comprehensive that it is on a very solid foundation.

Until comparatively recently, it has been a disconcerting feature of general plastics activities to imitate other materials. As a consequence this has led to much criticism and an implication of inferiority. Fortunately the trend to apply plastic materials along lines suggested by their own intrinsic properties—on a purely functional basis has now become well established.

In the United States in particular, the subject of plastics has been discussed to such an extent in the press, the magazines, etc., that the public has become acutely conscious of the merits of plastics. A clear realisation of the merits of the materials is largely a matter of correct education. It cannot be too strongly impressed that the various materials used in the plastics industry have excellent properties which do many jobs superlatively well, and which fall in with the modern trends of production technique and performance. On the other hand it cannot be over-stressed that the use of plastics is not an absolute guarantee that some difficult job may be performed. It is all a question of perspective. Plastics will certainly not replace all existing materials for every task. Some materials they cannot replace for any task. It is essentially a matter of selecting the right plastic to perform a function for which it is suited.

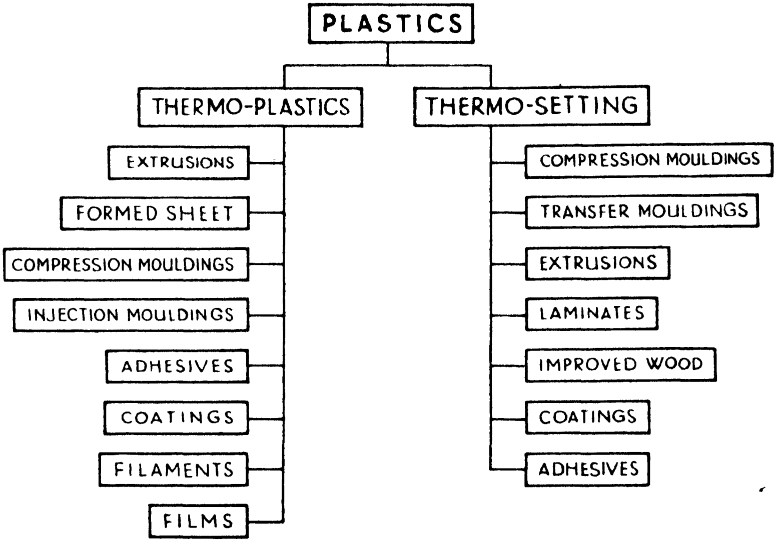


Fig. 2. Forms in which Plastics are available

The Make-up of the Industry. The constitution of the plastics industry has become quite complex. A consideration of the basic fabrication processes illustrates this.

Apart from the nature of the materials there are clearly many other factors which contribute to make up the plastics industry. For each type of plastic there are the initial raw materials concerned which have to be converted into a suitable condition by the chemical industry. Vast quantities of specialised equipment is involved in the conversion of these raw materials into the intermediate chemicals, and then into the actual synthetic resins, and finally into plastic materials ready for fabrication. All the knowledge and resources of the chemical engineering industry have to be utilised. Then again the handling of the plastics themselves in the preparation of commercial articles is also normally carried out by specialised concerns who are equipped with the most suitable plant. Consequently the plastics industry, as such, has many interested contributory parties. For example, long before the general public comes into the picture as consumer of the various products, the materials may have been dealt with in turn by the raw material industry, the chemical industry, chemical engineering, plastic manufacturers, plastic engineers, and the fabricators. It is quite evident that here there is the possibility of a complex industry capable of integration. Indeed this trend for the co-ordination of numerous small units into large integrated firms is already well under way.

TABLE 5

RELATIVE USE OF PLASTICS, 1946

Type of Usage	Production, 1,000 lb.	Percentage of Total
For protective coatings . . .	379,800	38·2
For moulding and casting . .	245,000	24·6
For laminating	36,700	3·7
For adhesives	78,000	7·9
For treatment of textiles, paper and leather	46,300	4·7
For ion exchange	1,200	0·1
For miscellaneous uses . . .	207,000	20·8

So far as the plastics themselves are concerned, there are two principal divisions—the manufacture of the plastics materials, and the moulding or fabricating of the plastics. This is best illustrated by considering the manufacture of phenol-formaldehyde resins. The company purchases phenol and formaldehyde and converts these into resins. It blends the resins with filling materials and colours, and prepares its final product as a coloured powder. This concern does not normally mould the materials. It sells the powder at a price which may range from about £50 per ton upwards to firms who specialise in moulding.

These trade moulders have all the necessary equipment such as presses and moulds, and also have the necessary experience of moulding. Their business is, in general, based on many orders for long runs of products. This very facility for mass production, conforming to modern trends, largely accounts for the growth of the industry. It is necessary to mould many thousands of the same article in order to cover such items as mould costs, which are very high. The moulded product is either an accessory, a part of some other product such as an electrical component, or it may be a finished product such as a cigarette box.

There are comparatively few concerns who make the phenolic moulding powders and also mould them. Mention of processes and moulds introduces two other important sections of the industry, the manufacturers of presses and accessory equipment, and the quite separate engineering activity of mould design and manufacture.

Apart from concerns whose specific function is either the preparation or fabrication of articles from plastics, there is a steady trend for large industrial concerns to instal either resin production units or moulding units. In these cases there is a specific internal demand for large quantities of plastic articles which justifies the creation of a special plastics division. Any excess capacity often leads these firms to produce articles for the open market.

While the references in this analysis have applied to phenolic resins the same holds good for other forms of plastics. For example, cellulose plastics are, in general, prepared from raw material by specialised firms, while the fabrication into finished articles is carried out by other concerns.

Historical Background of Industry. The plastics industry is not a new industry, although it has expanded beyond all recognition during the last twenty years. It is mainly based on a number of synthetic resins and a group of cellulose plastics. On the other hand, bitumen and casein have been known since Biblical times. Nitro-cellulose moulding is already some eighty years old. Yet understanding of these materials has only come about comparatively lately. In particular the recognition of synthetic resins as useful commercial materials has only come about in recent years.

The history of organic chemistry, particularly during the last century, shows that all experimental work was accompanied, and hindered, by the formation of tarry resinous masses. These materials appeared to have no uses. Chemical technique was inadequate to handle them. They were given scant attention, being considered a nuisance. In recent years, with a growing understanding of various phenomena, it it has been possible to re-examine these waste materials more closely and one result is that the plastics industry has expanded out of all recognition.

In spite of this generalisation it is a fact that numerous alert chemical workers noted among these seemingly useless materials unusual behaviour, which at the time they could not usefully employ. In many cases the time was not ripe. The other essential contributory factors, notably the manipulative technique and the necessary equipment, were not then available. Neither was the main driving force present, namely, industrial demand for such materials. The conditions were simply not right for their arrival. So it happens that many of the newest forms of plastics are rediscoveries. This may cause great surprise. They are none the less meritorious, nor does this fact detract from the credit due to the latest workers. For it is a far cry from a laboratory material to the commercial product. A typical example is polystyrene, which was first discovered in 1835. Another is polyvinyl chloride. The same might be said about the cellulose plastics.

Another interesting feature is that one of the primary causes for the arrival of plastics has been the frequent endeavour to replace natural materials which happen to be in short supply. This became a major consideration during the war, and it is still an important factor. For example, nitro-cellulose plastics arrived to replace ivory. Casein, too, was connected with a similar problem to replace horn which was in short supply. In the early days of this century much of the drive behind the phenolic resins was directed at replacing shellac. With the recent war-time necessity to replace tung oil, natural resins, and other natural materials, this urge has recently become even more emphatic. In fact, at the present time it is stronger than ever. Many plastics are being developed at a rapid rate in order to make good the shortages of fabrics and metals. Polyvinyl chloride is the outstanding example of a material which has come into wide use to replace rubber and fabric. Moulded plastics replace brass, copper, steel, etc. So through one cause or another these synthetic products develop along a long road of endless improvements.

It is of the greatest interest in this connection to notice that the same trend is marked inside the plastics industry; that is to say, that one plastic will tend to replace another when the properties of the newer one become more attractive. Oddly enough this has not had the effect

TABLE 6
PROGRESS IN PLASTICS

1875	Celluloid	Sheets, rods, tubes
1901	Alkyd resins	Solutions
1904	Casein	Thick sheets, rods
1909	Phenol-formaldehyde	Castings
1911	Cellulose acetate	Sheets, rods, tubes
1912	Modified alkyd resins	Coatings
1919	Vinyl acetate polymers	Adhesives
1922	Phenol-formaldehyde	Laminated sheets
1924	Phenol-formaldehyde	Moulding powders
1924	Urea-formaldehyde	Cast forms
1929	Urea-formaldehyde	Moulding powders
1929	Modified vinyl acetate	Powders, films, sheets
1931	Acrylic esters	Castings, mouldings
1931	Phenol-formaldehyde	Modified cast resins
1931	Urea-formaldehyde	Laminated sheets
1932	Methacrylic esters	Castings, mouldings
1933	Polystyrene	Moulding powders
1933	Cellulose acetate	Injection moulding powders
1933	Benzyl cellulose	Sheets, rods, tubes
1934	Celluloid and cellulose acetate	Continuous extruded sheets
1935	Vinyl chloride polymers and copolymers	Sheets, rods, powders, films
1935	Polyamide resins	Flakes, filament
1936	Phenol-formaldehyde	Extruded tubes
1936	Polyisobutylene	Slab
1936	Ethyl cellulose	Sheets and powder
1936	Polystyrene	Transparent moulding powders
1937	Urea-formaldehyde	Transparent moulding powders
1937	Polyethylene	Rods, tubes, sheets
1938	Casein	Injection moulding powders
1939	Melamine-formaldehyde resin	Solutions, moulding powders
1939	Polyvinyl butyrate	Sheet
1939	Cellulose acetobutyrate	Moulding powders
1940	Polyvinylidene chloride	Extrusion of filaments
1942	Polyamide	Moulding powders
	Silicone resins	
	Polyesters	

of eliminating many plastics, for whenever one market is lost, another is found which more than makes up for the deficiency. The outstanding example is cellulose acetate. Having lost the safety glass market to polyvinyl butyral, injection moulding expansion has caused an enormous demand, far outstripping the lost field. Nitro-cellulose plastics still thrive in spite of their disadvantages.

The plastics industry of to-day is built on the foundation of Baekeland's work on phenolic resins, but each commercial plastic as developed is evolved from a large volume of work carried out by numerous scientists and technicians in every part of the world. This applies even in the case of phenolic resins, although these are invariably associated with Baekeland.[1] He was one of many workers on the subject, although it is still true to say that his work was the focal point of the whole industry.

Phenolic resins, as such, were already known some forty years before Baekeland. He brought them out of the nebulous clouds of the chemical laboratory. He showed how to make reproducible products, how to conduct the process and how they could be made commercially useful. Earlier workers may have made some contributions to the subject, but his were the key contributions.

There is always an element of good fortune about industrial development. For example, the merits of phenolic resins for moulding would undoubtedly have become fully recognised in due course. The development was accelerated by the demands of the radio industry in 1922. Each industry in turn helped the other. In a similar way, the excess cellulose acetate available after the last war led to the acetate rayon industry. More recent examples of circumstances forcing the development of plastics include the war-time pressure on polythene, methyl methacrylate polymer and polyvinyl chloride, and the requirements of the synthetic rubber industry performed the same function for polystyrene.

The Development of the Plastics Industry. The plastics industry in its present form can only be regarded as about twenty years old.

Twenty years ago there were some materials which became plastic when heated and could be converted into commercial products by moulding or by extrusion. Familiar examples include shellac, which was being used to make gramophone records, and for insulation, while casein was employed for making buttons, pens, pencils, and many other decorative articles. For electrical purposes the outstanding material in general use was ebonite. This suffered from the great disadvantage that production was difficult and slow. Ebonite was consequently expensive. Celluloid was very widely used despite the uneasiness caused by its inflammability.

At that time vague stories were being circulated concerning a mysterious synthetic resin which was reputed to give remarkably moulded electrical parts of unusual complexity of form. It was at this time that wireless transmission and reception became general. An enormous demand arose for wireless sets. Mass production was essential to satisfy this demand. Many millions of parts were required for these sets. The essential features were that these parts should be made quickly and cheaply, and yet have the essential electrical and mechanical properties for application in wireless sets.

Waiting to fulfil these requirements was a synthetic resin—phenol-formaldehyde resin. It stepped into the breach and triumphantly met every necessity. It was the ideal material for the mass production of small moulded parts. In a very short time phenol-formaldehyde resin, in the form of moulding powder became the foremost insulating material. It ousted ebonite from the position of monopoly it had long maintained. This was an epoch-making development, for it marked the real beginning of the plastics industry. Obviously, while radio provided the industrial *entré* for phenol-formaldehyde resins, yet in turn these resins have contributed greatly to the subsequent development of the electrical industry. The presence of this plastic material which could be moulded with such ease had another profound effect.

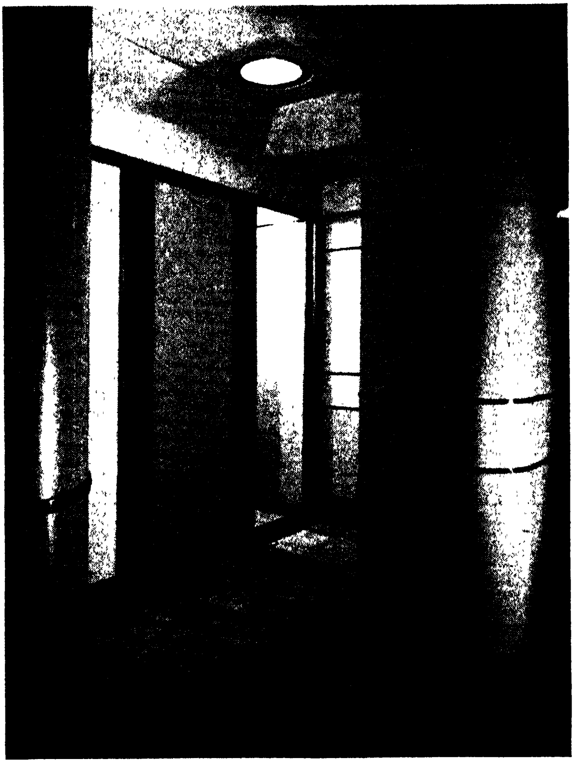


Fig. 3. Wall surfaces composed of phenol-formaldehyde veneer[9]

It provided a nucleus around which the other unassociated plastic materials could crystallise to form the plastics industry.

During the last ten years the plastics industry has been enriched by numerous new materials. The spectacular arrival of new synthetic plastics and rubber-like materials during these years has been most impressive. It is notable that prior to this, most commercial plastics were obtained *via* a condensation process. During this period the outstanding new plastics have been those products obtained by polymerisation. There is almost a clear line of demarcation.

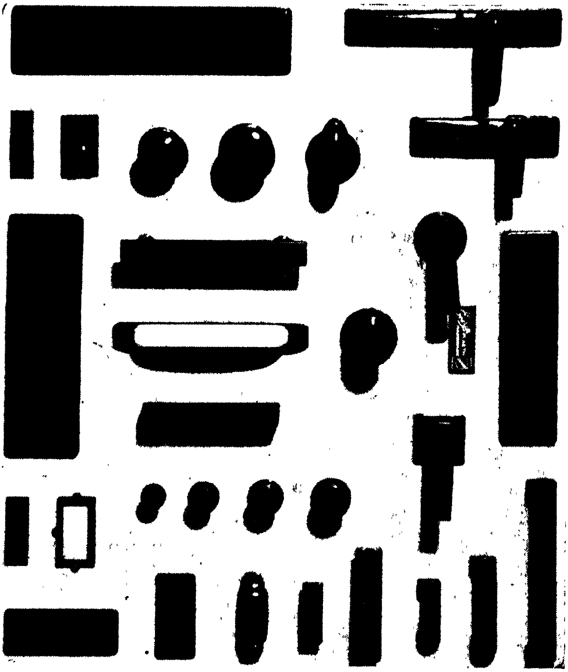


Fig. 4. Widely used moulded door furniture[9]

Many of these polymerisation plastics have already achieved great industrial importance. Numerous others promise to do so. So far as any general classification is possible, the important groups are synthetic resins derived from acetylene and ethylene, known as the ethenoid or vinyl resins, and the synthetic rubber-like materials. They all have many features in common, and actually represent the transition from plastics to rubber.

Important ethenoid resins include polyvinyl chloride, polyvinyl acetate, polyacrylic acid esters, polymethacrylic acid esters, and nitriles, amides, acetals, etc.

The Growth in the Size and Scope of Plastics Articles. Until comparatively recently, plastics were confined to the production of small articles. Everyone is familiar with the innumerable gadgets made

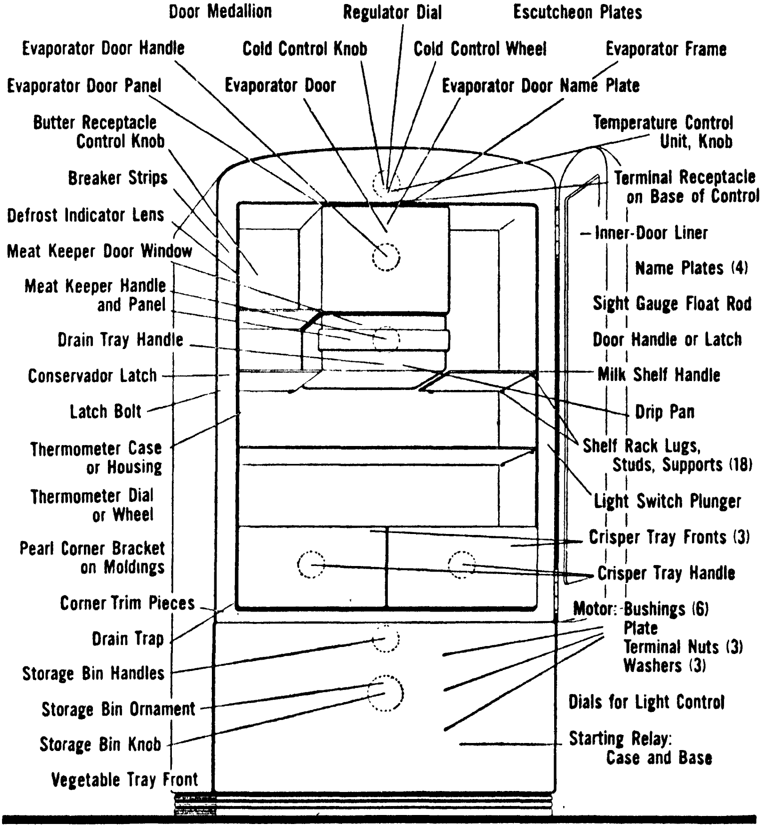


Fig. 5. Plastic applications in a modern refrigerator[11]

by moulding plastics. The Americans have an innate craving for gadgets. Plastics are admirable for making such gadgets on account of their colour possibilities, together with the fact that they can be handled by mass production methods. But in recent years a turning point has come in the industry. Plastics are on the verge of becoming structural materials or component parts of structures. This is of the most profound significance. It opens up far wider possibilities than were ever envisaged. It makes possible the idea of prefabrication of numerous essential structures such as houses, etc. The application of plastics as stress-bearing materials is already a reality. On the other hand, it would be foolish to imagine that anything like finality has been reached. That is not so.

There are close connections between plastics and other industries. For example, cellulose plastics owe a great deal to the rayon industry. In turn, the rayon industry draws on new plastics as raw materials for new fibres, and on older types of plastics for equipment. The same applies to the film industry. All the coating industries making paints, lacquers, etc., owe a great deal to the evolution of plastics. Complete plastic coatings have been developed and are giving satisfactory service.

The Spread of Plastics. Plastics impinge on every aspect of human activity. The extent is almost bewildering. It is not an industry where one can say that any single material or article predominates in the way, for example, that tyres predominate in the rubber industry. This diversification has a great stabilising effect.

Although phenolic moulding plastics have been the leading products so far, and still enjoy the largest volume of application, others are approaching it in output; notably vinyl plastics and cellulose plastics. It is a fact, for example, that plastics used by injection moulding are still virtually at the beginning of their expansion.

To consider applications of plastics is almost to present a catalogue. Perhaps the best approach is to consider plastics in daily life. One can start a day with a tooth-brush made of one of the many types of plastics, with nylon bristles to complete the assembly. The bathroom fittings, shower-bath surrounds, the curtains, etc., will probably be made of plastic materials. Dentures and spectacles may be of acrylic plastics. The tooth-paste would be in a container almost certain to be capped with plastic. The average dressing-table abounds with outstanding examples of articles fabricated from plastic.

In the case of a man his shaving-brush and shaving-soap containers and razor would be almost totally plastic. Numerous clothing accessories, including collars, braces, or suspenders, boots and shoes, jewellery, etc., will also be made of plastics.

Furniture may well be either plastic or plastic-bonded wood, and this may quite likely apply to interior decorations and fittings. It goes without saying that in these days electric switches and fittings will almost certainly be moulded. The probability is that this applies to lamp shades too. Dressing-table fittings, chair covers, and so on, will also come into the same category. Telephone and radio sets are outstanding examples of plastics.

Although plastic cups and saucers have not gained popularity for general use, nevertheless they are used to a great extent, especially for secondary purposes. During the war emergencies they were widely used in place of pottery, which was not available. However, other accessories for the table such as condiment dishes, various containers, etc., are certainly made of plastics, The handles of knives, forks, spoons, and so on, are also of this type. The kitchen is full of typical plastics articles. Present-day refrigerators and accessories are outstanding examples of the extent to which this trend has gone.

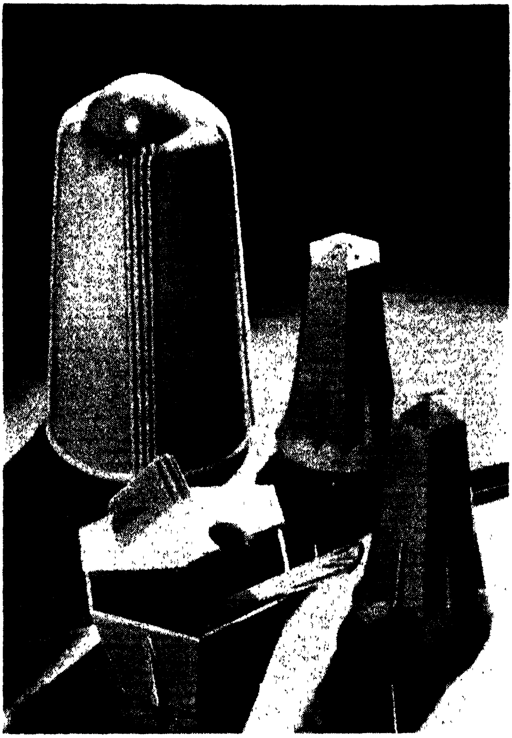


Fig. 6. Typical mouldings from urea-formaldehyde moulding powder[10]

So one might go on almost indefinitely. Accessories of leisure, such as playing cards, chess men, chips, etc., are in the plastics orbit. The nursery, too, nowadays contains numerous examples; there is a wide variety of toys and bricks, and decorative articles of every description.

Out of the home, in office or factory, the same is still true. Office equipment and gadgets of every description abound. Process machinery parts, bearings, gear wheels, and gadgets are found in nearly every works irrespective of the type of product being made.

Once one becomes aware of plastic materials, they are encountered in every phase of human activity.

The industrial uses of plastics are manifold. In many cases they are hidden from sight, and the casual onlooker is not aware of them. In fact, by far the greatest amount of plastics articles are in machinery parts, factory equipment, and electrical equipment, well away from the general view.

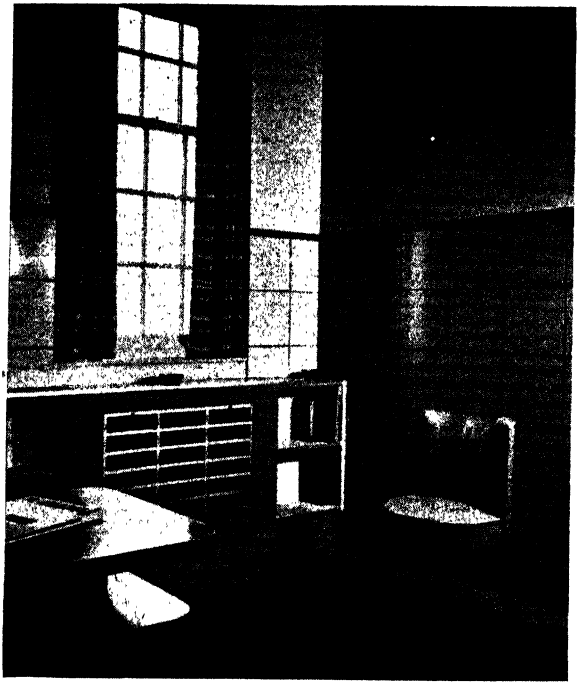


Fig. 7. Modern office, showing wall surfaces, underledges, table-tops having resin-treated veneers[9]

The emphasis varies in different countries. In this country plastics have been used carefully as relatively expensive materials. By contrast for many years the Germans have concentrated on employing plastics as cheap materials in every form of machine to displace metals; in agricultural machinery, in aircraft parts, etc.

American activities, until they entered the war, were mainly directed to the more spectacular luxury articles of less utilitarian application. These articles have been made by the million, forcing the development of mass production methods. Enormous enthusiasm had been generated. The materials had begun to satisfy many industrial desires and requirements.

American use of plastics since the end of the war has expanded in a most extraordinary manner with demand far outstripping supplies. Enormous outlets are found in the fields of synthetic coatings, synthetic fibres, electrical equipment, car, railway and steamship production, refrigeration, plumbing, house construction, packaging, and furnishing, etc.

It is amazing to contemplate how diverse plastics spread unrecognised through aircraft, battleships, tanks, and the entire run of military equipment. Plastics swung into war production with amazing celerity and success.

The Appeal of Plastics. What is it that plastics materials have? They combine a number of desirable inherent characteristics, and the fact that they lend themselves to mass production operations or continuous operations. The inherent properties by and large include the complete colour range in both opaque and translucent effects, and also materials with the best known light transmission.

Superb electrical characteristics are available if desired, and this is accompanied by toughness and flexibility.

Another general attribute is their lightness as compared with other materials. It is also a fact that their durability is outstanding. They soften at temperatures low enough for easy manipulation, but high enough to maintain rigidity at working temperatures. They are transparent like glass, but not brittle; they are light like wood, but have no grain, and can be cemented; they are coloured and non-corrodible like ceramics, but tough; they can be highly elastic, like rubber, but stable in the atmosphere and do not require vulcanisation; they can be like leather, but are rot-proof and practically indestructible; in fact, they compare favourably with almost everything except the heavier materials of construction.

There can be no shadow of doubt, however, that the best value of plastics will only emerge when articles or structures are specifically designed for them. Their leading virtues, such as light weight, ease of fabrication, fatigue strength, colour possibilities, and so on, can then be used to maximum advantage. Although plastics are so very versatile, much more so than metals, yet their disadvantages as well as their advantages must be considered. They cannot be accepted as panaceas for all difficulties.

All the desirable characteristics for some particular purpose may not be present in any one plastic. The ideal plastic has yet to be found. But generally, each material will have one or more outstanding feature.

Moreover, they are all the time being continually made better. Various defects are being eliminated as more is being learned about the nature of the material. For it is a sobering fact that not a great deal is known about the structure of most plastic materials.

Another important feature is that as the demand and output of these materials increases, so they become cheaper.

The Application of Plastics for War Tasks. Plastics played an outstanding part in the production of war equipment. They played a very important part as a means for replacing such materials as were in short supply owing to the war; for example, rubber, metal, glass, and so on. In such changes it has become evident that their production can be brought to an extremely efficient state.

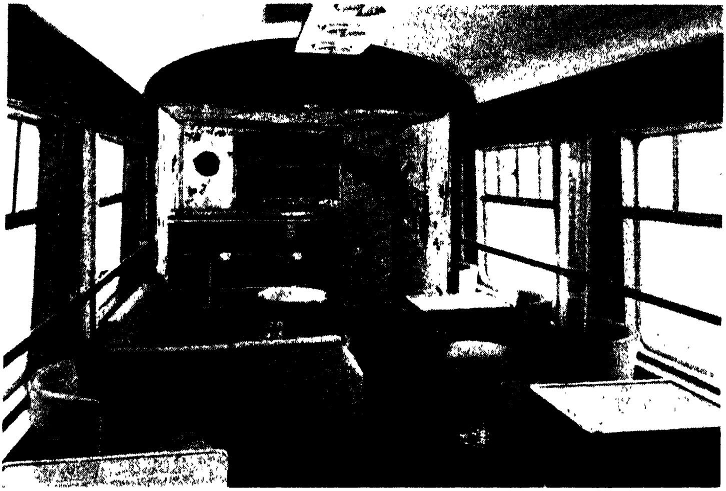


Fig. 8. First-class lounge of the Coronation Scot, showing tables and wall surfaces incorporating inlaid designs[9]

Many of these developments are here to stay, irrespective of war conditions. The large-scale manufacture, necessary to war production, has served to bring down the cost, and has made them more competitive with the materials which they have temporarily replaced. They made good a number of shortages of other materials, notably rubber and metals. Plastics of one sort or another, moulded, extruded or as cements, have been used as accessories in every machine of war. In many instances their own inherent properties account for their application under the most arduous conditions. For some uses their weight-saving characteristics is a predominating consideration.

Many spectacular war uses are familiar to everyone. For example, the use of transparent sheetings, such as "perspex" and cellulose acetate in aircraft. The appearance of innumerable familiar moulding components and accessories are likewise everywhere to be seen. But apart from the spectacular and familiar applications, the uses of the different plastics are legion, and in many cases are not realised. The electrical field, and notably communications, is clearly dependent on plastics in its cables, batteries, telephones, microphones, and the other accessories too numerous to detail.

Fig. 9. The outstanding war-time phenolic moulding. The "69" hand grenade, made up of seven mouldings[10]

Some idea of the part which plastics played in war production may be gained by considering their uses for aircraft alone. Many of these applications have carried over into peace-time conditions. It is a fact that many airplane parts are now being made of plastic-bonded plywood. These include fuselages, wings, elevators, flaps, ailerons, stabilisers, nacelles, bomb doors, floats, controls, rudders, taps, spars, rigs and propellers. Other portions using laminated materials include ducts and pipes for ventilators, pilot-seats, cabin partitions, doors, floorings, and so on.

The widespread use of transparent plastic materials is of course well known. Either acrylic resins or cellulose acetate are employed to make cockpit covers, gun turrets, astradomes, blisters, windows, etc., in nearly all aircraft. When one considers the field of moulded articles, their number is almost legion. In common with ordinary trends in electrical equipment, such things as circuit breakers, switch boxes, switches, panel boards, sockets, connectors, terminal boxes, switch-box covers, junction boxes, etc., are all moulded from either phenol-formaldehyde resin, urea-formaldehyde, or melamine resin. They combine electrical requirements with lightness and great strength. Insulation of

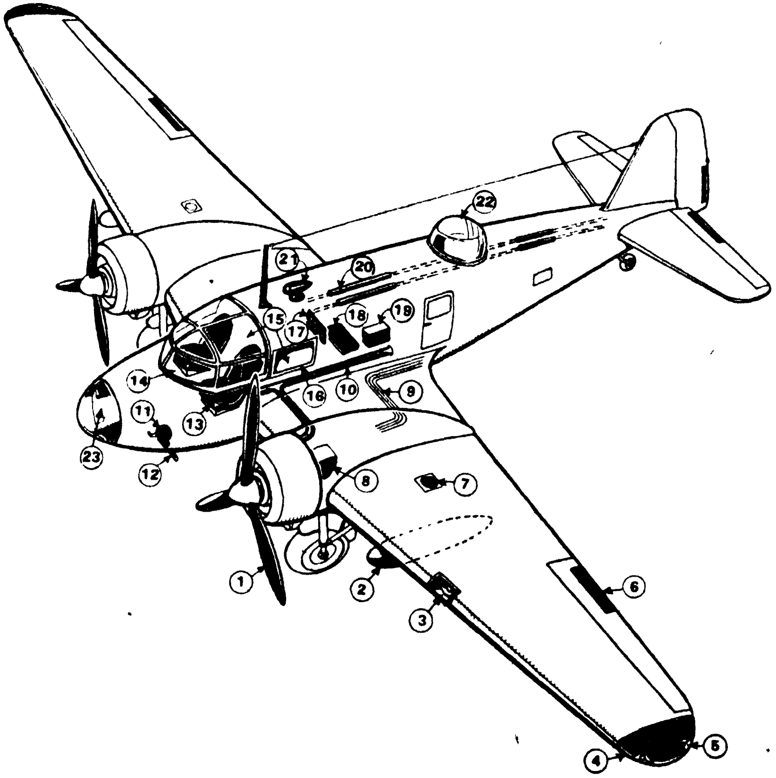


Fig. 10. Diagram indicating the uses of plastics in aircraft[11]

1. Airscrew blades and spinner
2. Jettisonable fuel tanks
3. Landing light shield
4. Wing tips
5. Navigation light covers
6. Trimming tabs
7. Tank fillers
8. Hydraulic liquid header tank
9. Cable conduits
10. Air ducts
11. Radio antennae reel
12. Antennae lead-in tube
13. Pilot's seat
14. Windscreen
15. Window or cockpit panes
16. Window frames
17. Radio panel
18. Table tops
19. Battery case
20. Control wire guards
21. D/F housing
22. Turret
23. Nose window

wire and cables is largely based on polyvinyl chloride or copolymer plastics. It is fairly evident that numerous other gadgets such as knobs, handles, switches, panels and dials are moulded from either thermosetting or thermoplastic materials. For operational night flying, illumination of panels, switches, indicators, dials and charts is achieved by the use of fluorescent plastic sheet, and plastic materials which have the characteristic of edge-lighting.

If one may mention a few other items, such as tubes made of polyvinyl chloride, artificial leather for upholstery made with vinyl chloride acetate copolymer, machine-gun feeding rollers moulded from cellulose plastics, etc., it becomes quite evident that plastics play an extremely important part in aircraft at the present time. The description of applications in other branches of war application is equally impressive and lengthy.

Considering some of the leading materials, phenolic resin mouldings are put to direct military use in such articles as grenade parts, shell noses, bomb parts, aircraft fittings, ship fittings, and fittings on vehicles of every description. In aircraft, parts of the ignition system, a variety of pulleys, fair leads, and so on are used. Packages of every description, and items such as buttons, etc., are a few of the abounding examples of phenolic mouldings. They feature in all the housings of instruments, all the electrical parts of the various equipment.

Phenolic laminated materials play a more spectacular part. They feature in the form of moulded aircraft, ranging from large parts of the monster machines to the Mosquito bomber, down to the humble training plane. The components may range from fuselages to wings. They play a great part in the production along mass production lines of plastic-bonded torpedo-boats and small craft of every description. They play a part in the fittings of aircraft, ships, and vehicles. Gas masks, bugles, bayonet scabbards, helmets, feature among infantry equipment, the soldier's numerous personal items are also largely based on plastics.

In the background behind the fighting lines there was an enormous application of phenolic resins. The whole range of industrial products and machine tool parts, accessories, such as gears, bearings, and so on, are typical examples.

The urea-formaldehyde resins have played their greatest part as adhesives for plywood. As mouldings they have featured in the production of utensils, both for the armed forces, and the civilian population.

Vinyl resins made spectacular contributions to the war effort. As insulation to replace shortages of rubber they have proved remarkably successful. Their use is expanding by leaps and bounds. Their importance on military communications need not be emphasised. Some types of these plastics were used for coating fabric for army clothing, etc., and waterproof equipment. Other types were used for instruments, etc. In the same field plastics such as polyvinyl butyral are also being effectively used as a rubber substitute, particularly for proofings and adhesives. They also feature in bullet-proof glass. Acrylic resins played an outstanding part in the war, chiefly in the form of transparent sheeting for aircraft. Apart from these uses, however, they are employed for lenses, dentures, corrosion-resisting containers, for the treatment of fabrics, and so on.

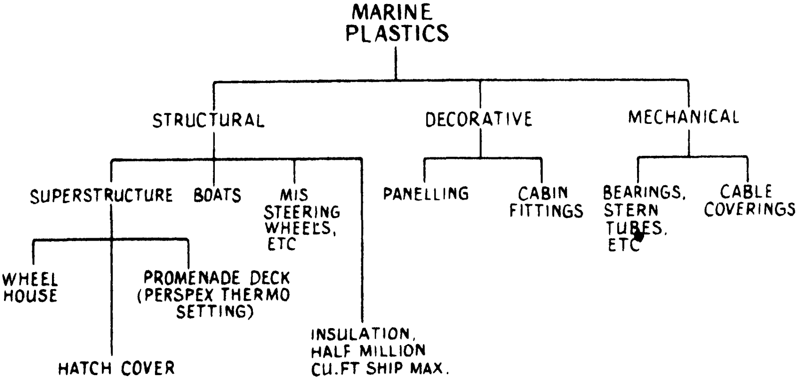


Fig. 11. The main groups of marine applications of plastics

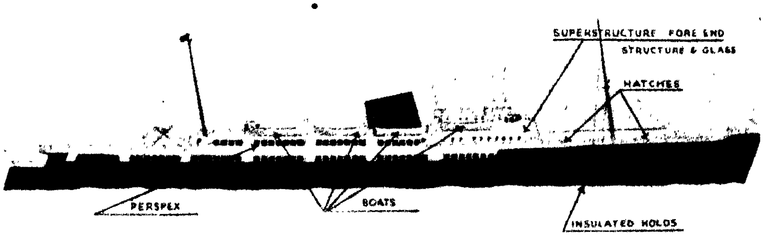


Fig. 12. Modern passenger packet, showing possible plastic applications. She is "glazed in" for more than half the length[10]

Polythene is of primary importance in the field of communications. Polystyrene, too, is playing an important part in this field. The cellulose plastics feature not only as film base, but in the production of innumerable accessories made by injection moulding. Such military examples as steering wheels, handles, and accessories on guns, gas-mask accessories, aircraft parts, and a thousand and one other uses.

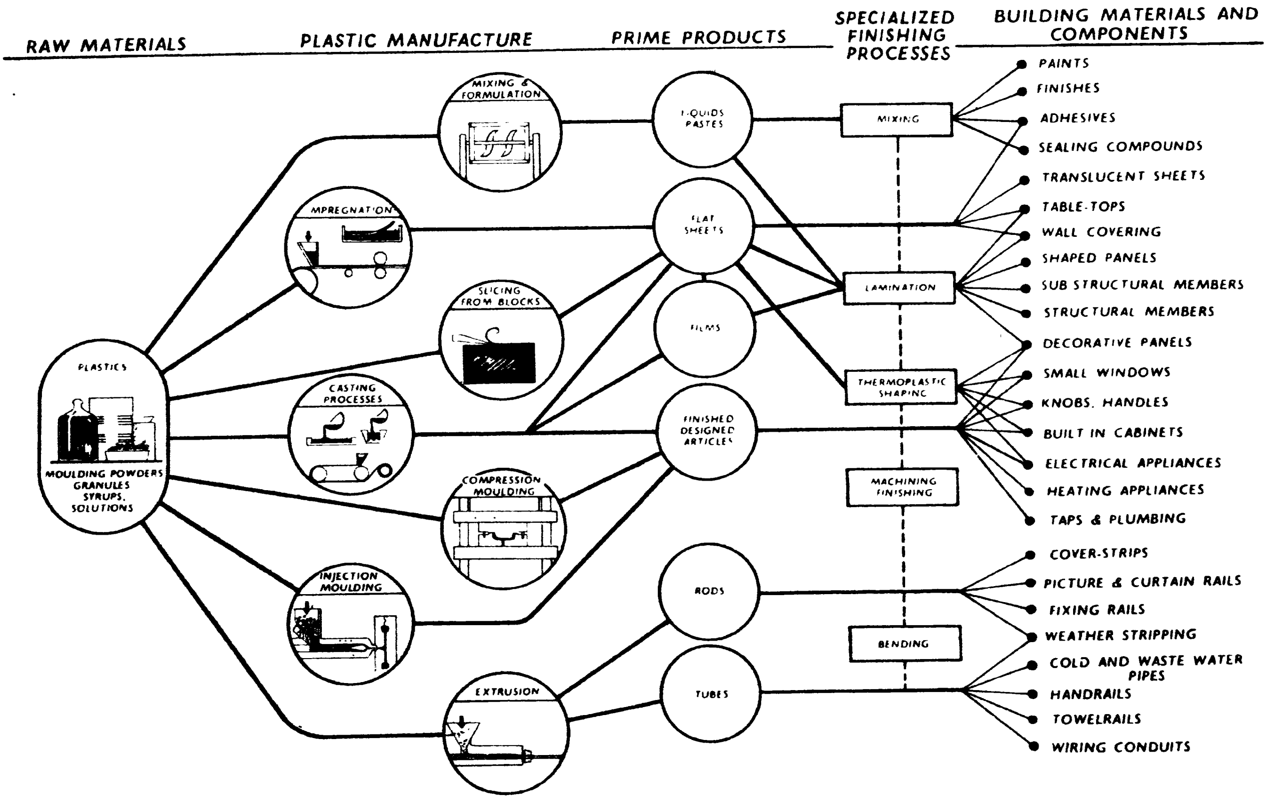


Fig. 13. Plastics as building materials[3]

The Future of Plastics. Yarsley and Couzens[8] have stated that "Plastics will bring new products and new standards of hygiene and colour into the life of everyone, and corrosion and decay to which we have long been accustomed with conventional materials will be reduced to a minimum. New types of architectural materials can speed up production, and the exploitation of the remarkable properties of plastics products should give rise to new members of construction."

The use of plastics may enable the production of lighter and stronger structures at much lower costs than are at present available.

Future dwellings will undoubtedly be profoundly influenced by plastics. This angle has been admirably described by Fejer.[3] Fig. 13 succinctly outlines the possibilities.

Leading American car manufacturers appear to be satisfied that the evolution of car bodies will come into the plastics field.

Apart from this, plastics are already of great significance in the average motor-car. Once again this can best be brought out by a diagram. (See Fig. 14.)

Trends in marine design also suggest that plastics may attain considerable importance. Applications in luxury vessels of the past, may be forerunners of general practice in the future. Hardy[5] has studied this angle in relation to large vessels. The field of small craft is already invaded by plastic laminated materials.

Another point with reference to the future of plastics is that while the discussion so far is chiefly concerned with technical and utilitarian equipment, plastics have even wider horizons. The arts have a very great interest in them. There is much interest in design from the functional point of view. But an outstanding feature of most plastics materials is the unparalleled beauty of colour, surface, form, and texture. They lend themselves to every form of manipulation. As a result they are of interest to the creative artist, such as sculptors, painters, and commercial artists. Already there are many examples of exquisite and beautiful craftsmanship comparable with the best work in other media. There are all sorts of novel features about plastics, hitherto unavailable in other materials, which lend themselves to artistry and design. As outstanding examples, one might mention edge-lighting and curved-light effects of methacrylate resins and polystyrene.

Synthetic resins and plastics generally have an enormous future in the field of textiles. Here they find application in three ways. For many years they have been used as coating materials applied to textile fabrics to make artificial leather, oil cloth, tarpaulins, etc.

In recent years synthetic resins have been used to impregnate textile

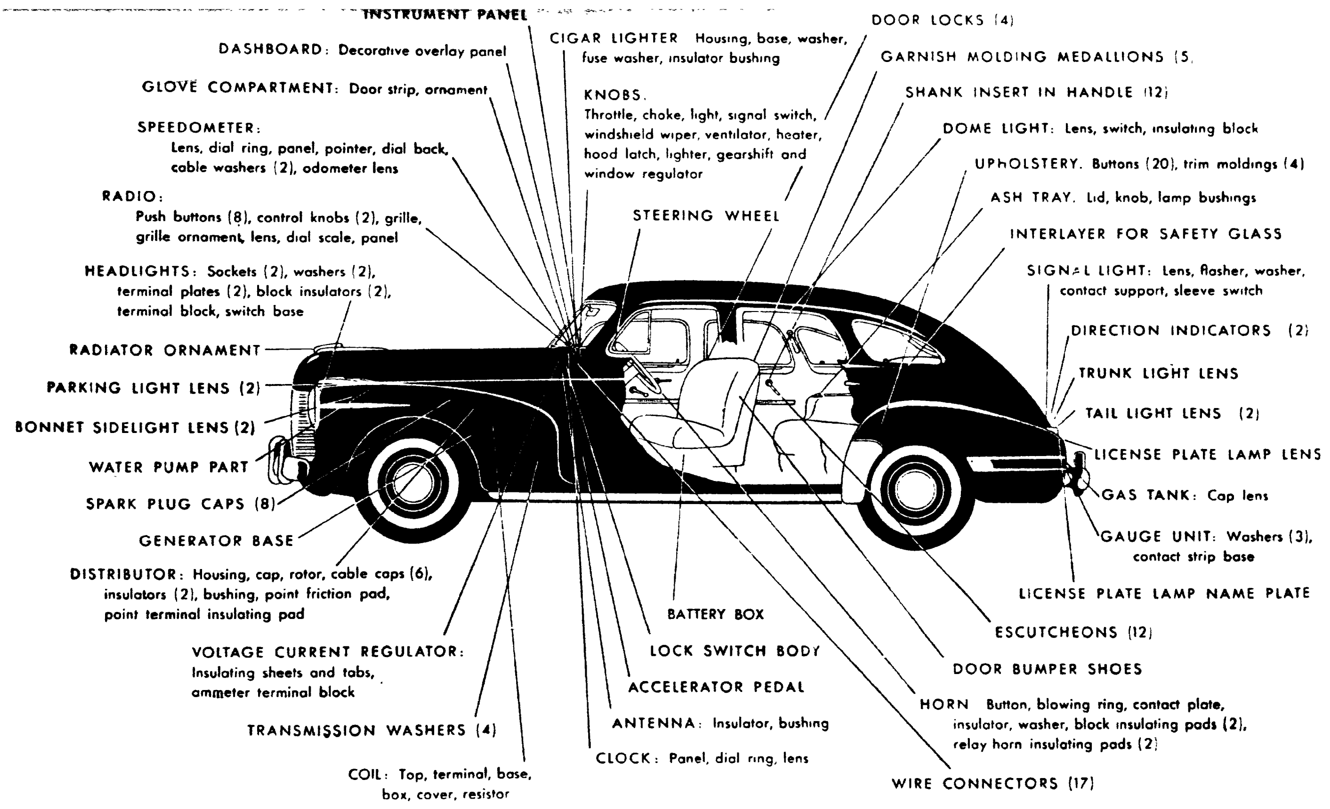


Fig. 14. Plastics applications in typical American car

fibres. The object has been to improve the physical characteristics without affecting the appearance. According to Powers:[6] "To-day there are fabrics which consist of 30 per cent synthetic resin and 70 per cent fibre, and yet they retain all of the appearance, feel and even microscopic characteristics of a textile fabric . . . to-day there are millions of yards of cotton, rayon, wool, and silk fabrics which have been modified and whose serviceability has been improved by the addition of 1 to 30 per cent of specially developed synthetic resins." Urea-formaldehyde resins and acrylic resins predominate in this field.

The third aspect is, of course, the use of synthetic resins and their plastics actually to make synthetic textile fibres of outstanding character. The cellulose fibres are well-established rayons. Nylon is in every-expanding production. Vinyon and saran fibres are freely available. The trends here are all steeply upward.

Plant required for Plastics. The plant used in the preparation of plastic compositions and the fabrication of finished articles is largely based on types existing in other industries. The ready availability of plant which can be adapted for use with plastics is a contributory factor in the rapid expansion of the industry.

Mixing equipment involves such items as powder mixers, and dough mixers which are used in many light industries. Heavy duty internal mixers, and mixing rolls have been borrowed from the rubber industry.

Presses of every description are employed. Special plastic types have been evolved which are rather more effective than the original presses borrowed from the rubber industry. For thermoplastic materials, as with rubber, calenders are employed to make fine sheetings and to coat fabrics, etc. Extrusion of thermoplastics has until recently been carried out on machines designed for rubber. Now specially designed extruders are coming into use. Injection moulding equipment is based on metal casting plant, although the machines have now taken on their own specialised character.

TABLE 7

MACHINES IN THE U.S. PLASTICS INDUSTRY

	1941	1944	1947	1948
Compression presses	8.000	11,500	13,250	13,600
Injection presses	1,000	1,500	3,500	4,000
Extruders	—	350	1,250	1,400
Extruders for wire coating . .	—	330	—	—

Apart from these, in the fabrication of various plastics products the whole range of woodworking and engineering tools is used. The leading items are described at appropriate points in the text.

Some indication of American potential so far as plant is concerned may be derived from the figures given in Table 7 (see previous page).

REFERENCES

1 Baekeland, *Ind. Eng. Chem.*, 1909, **1**, 149.
2 Carleton Ellis. *Ind. Eng. Chem.*, 1936, **29**, 1140.
3 Fejer. *Plastics*, 1942, **6**, 180.
4 German Consumption of Plastics. *Kunstoffe.* April 1940.
5 Hardy. *Plastics*, 1942, **6**, 57.
6 Powers. *Ind. Eng. Chem.*, 1940, **32**, 1543.
7 U.S. Consumption of Plastics.—U.S. Tariff Commission.
8 Yarsley and Couzens. *Plastics*, Penguin, London, 1941.
9 Illustrations by courtesy of Bakelite, Ltd.
10 ,, ,, British Industrial Plastics, Ltd.
11 ,, ,, *British Plastics.*

CHAPTER II

RAW MATERIALS FOR PLASTICS

THE plastics industry has expanded at an enormous rate and the numerous individual plastics have been derived from a variety of raw materials. In the past most interest has centred around coal-tar and cellulose as primary sources of its raw materials. However, the range is now very much wider than this. The raw materials used in the making of synthetic resins have mostly been obtained from among the following natural products: coal, cellulose, salt, sulphur, water, air, and limestone. To these must now be added petroleum and agricultural products, as major sources. The development of waste product from petroleum has been most spectacular during the last few years, and even greater developments are impending.

If U.S. plastics consumption in 1939 is taken as 100, in 1947 cellulosic moulding materials are at 750.

Phenolic Resins	300
Urea Resins	300
Melamine	300
Polystyrene	12,500
Vinyl Resins	15,000

The wedding of agriculture to industry has attained greatest success in the field of plastics. Henry Ford was one of the most enthusiastic and successful exponents. However, the soya bean around which most of his interest has been centred is merely one of a large number of agricultural products which are playing an important part in plastics production. Soybean plastics have already entered the field. Brazil is keen about a large programme for the production of plastics from coffee. Patents appear in great numbers for the production of plastics from cottonseed hulls, corn proteins, and bagasse. In the synthetic rubber picture, butadiene obtained from alcohol and other agricultural products is an accomplished fact. Waste sulphite liquors and scrap wood contribute large volumes of lignin plastics. Similarly, the plastics industry may expect to see a continued use of products derived from the rosin-turpentine field.

It seems the general practice that wherever there are waste materials an outlet is sought for them in the plastics industry, very often with notable and startling success. The conditions for success are quite clear: either a new product must have outstanding characteristics or be an abundant and cheap source of supply for older types.

The materials mentioned are the fundamental basic starting materials. Clearly a great deal of work has to be done to convert them into the physical condition and chemical composition suitable for conversion into the synthetic resin or plastic material. An enormous number of intermediate chemicals must be prepared, and in these processes large amounts of inorganic heavy chemicals must inevitably be employed. It should be well understood, therefore, that the preparation of plastics is essentially a chemical industry.

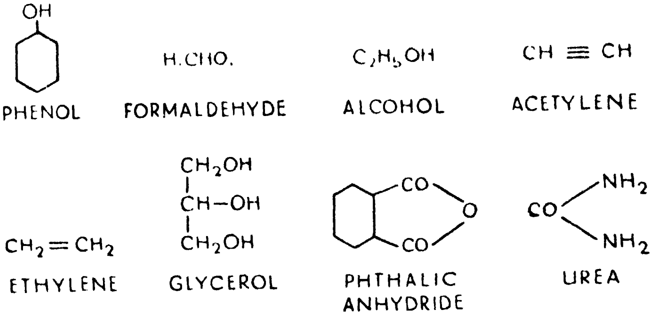


Fig. 15. Some leading starting chemicals

TABLE 8

QUANTITY OF THE MORE PROMINENT INTERMEDIATES USED IN PLASTIC MANUFACTURE IN THE U.S.

Chemical Intermediates	Quantity used in Plastics (in thousands of lb.) 1944	Percentage used in Plastics to Total Output 1948	Total Production 1944
Phenol	110,000	54·5	239,000
Formaldehyde	100,000	51·8	523,000
Urea	45,000	100·0	60,000
Phthalic anhydride	100,000	89·7	126,000
Glycerin	35,000	17·8	—
Acetic acid	40,000	13·7	1,595,000
Acetic anhydride	110,000	22·2	631,000
Acetone	30,000	7·8	450,000
Acetylene	113,000	28·0	—
Styrene	12,000	3·4	311,000

TABLE 9
SOURCES OF RAW MATERIALS

Plastic	Chemicals Involved	Source of Raw Materials
Phenol-Formaldehyde	Phenol	Coal Tar
	Formaldehyde	Coal Gas and Air, Wood
Cresol-Formaldehyde Resins	Cresol	Coal Tar
	Formaldehyde	As above
Phenol-Furfural Resins	Phenol	As above
	Furfural	Agricultural Wastes; husks, etc.
Lignin-Formaldehyde	Lignin	Agricultural Wastes; Sulphite liquor
	Formaldehyde	As above
Urea (Thiourea) Formaldehyde Resins	Urea (Thiourea)	Air; Coal Gas; Water (Sulphur)
	Formaldehyde	As above
Melamine Resins	Melamine	Cyanamide *ex* coal and limestone
	Formaldehyde	As above
Alkyd Resins	Glycerine	Animal Fats (also petroleum)
	Phthalic Anhydride	Coal Tar (via naphthalene)
	Maleic Anhydride	Coal Tar (via benzene)
CELLULOSE PLASTICS		
Cellulose Acetate	Cellulose	Cotton, Wood, Straw
	Acetic Acid	Coal via acetylene
	Acetic Anhydride	Natural gas via acetylene
Cellulose Nitrate	Cellulose	As above
	Nitric Acid	Air or Sodium Nitrate
Ethyl Cellulose	Ethyl Chloride	Petroleum via ethylene, Coal via ethylene, Agriculture via alcohol (fermentation), Brine
	Cellulose	As above
VINYL PLASTICS		
Polyethylene	Ethylene	Petroleum, Coal, Agriculture (fermentation)
Polystyrene	Ethylene	As above
	Benzene	Coal Tar
Polyvinyl Chloride	Ethylene or Acetylene	Petroleum, Coal, Agriculture
	Hydrogen Chloride	Brine
Polyvinyl Formal	Vinyl Acetate	Acetylene, Water
	Formaldehyde	As above
Polyvinyl Butyral	Vinyl Acetate	As above
	Butyraldehyde	Agricultural (fermentation)
Polymethyl Methacrylate	Acetone	Agricultural (fermentation) Petroleum
	Sodium Cyanide	Coal
Polyacrylic Resins	Ethylene	As above
Polyamides	Adipic Acid	Coal Tar
	Hexamethylene Diamine	Coal Tar
Casein	Casein	Milk, Soya Beans
	Formaldehyde	As above
Silicone Resins	Silicon Tetrachloride	Sand, Brine, Coal, Oil
	Grignard Reagents	

This table does not take into account the vast quantities of accessory heavy and fine chemicals involved in processing.

TABLE 10

UNITED STATES PRODUCTION OF CERTAIN SYNTHETIC RESINS IN 1947

Product	Production Pounds	Unit value cents./lb.
Resins from cyclic compounds		
Total	738,000,000	28
Alkyd Resins	283,000,000	36
Derived from coal tar	252,000,000	28
Phenolic and Cresylic Resins	—	—
For moulding	115,000,000	—
coatings	31,000,000	—
laminating	40,000,000	—
adhesives	32,000,000	—
Resins from non-cyclic compounds		
Total	514,000,000	51
Urea Resins	112,000,000	33
For moulding	50,000,000	—
adhesives	46,000,000	—
Polymerisation Resins	—	—
Polyvinyl Resins	177,000,000	39
Polystyrene	106,000,000	27
Polyethylene	15,000,000	50
Polymethacrylic Resins	15,000,000	—
Total for Resins, 1947	1,252,000,000	—
Total for Resins, 1944	784,000,000	—
Total for Resins, 1941	438,000,000	—
Total for Resins, 1938	130,000,000	—

The war has had a great influence on the expansion of the plastics industry. The much wider utilisation of plastics for high performance products has stimulated development to a considerable degree. To give one example, polyvinyl chloride has in the past been a high-price material. Shortages of standard plasticisers in Great Britain have forced great efforts to use other materials. As a direct result of the compounding skill attained, it is likely that polyvinyl chloride compounds will be far cheaper than was thought possible a short time ago.

Future Requirements of Raw Material. As a consequence of intensive work many new applications have been foreshadowed with the corresponding indication of enormously increased use of plastics in the future. The really large quantities which will be required make

Table 11

Plastics Materials Allocations in U.S.A.

1943 Volume (Plastics Resins and Raw Materials)

(all figures are in millions, except "unit cost")

	Total Pounds	Dollar unit, cost per lb.	Dollar value
PHENOL-FORMALDEHYDE RESINS .	283·4	0·24	68·01
Methanol	83·2	0·05	4·16
Formaldehyde	144·4	0·04	5·78
Hexamethylenetetramine . .	6·1	0·28	1·71
Benzene	109·5	0·03	3·29
Phenol	109·5	0·11	12·05
Substituted Phenols . . .	4·4	0·15	0·66
Ortho-Cresol	0·7	0·11	0·08
Meta-Cresylic Acid . . .	2·1	0·11	0·23
m-p-Cresols and Cresylic Acid .	17·5	0·18	3·15
Cresol and Cresylic Acid imported .	1·8	—	—
			31·11
CASEIN	41·7	0·25	10·43
Methanol	0·76	0·05	0·04
Formaldehyde	1·5	0·04	0·06
			0·10
ACRYLIC MONOMER AND RESINS .	36·4	1·00	46·40
Methanol	22·1	0·05	1·11
PHTHALIC ALKYD RESINS . .	147·1	0·30	44·13
Phthalic Anhydride . . .	49·0	0·13	6·37
Glycerine	26·4	0·17	4·49
			10·86
VINYL RESINS	86·6	0·615	53·26
Calcium Carbide	109·0	0·045	4·91
Methanol	1·60	0·05	0·15
			5·06
POLYSTYRENE	3·5	0·32	1·12
Styrene	4·2	0·28	1·18
NITRO-CELLULOSE	85·2	0·26	22·15

TABLE 11—(*contd.*)

PLASTICS MATERIALS ALLOCATIONS IN U.S.A.

1943 VOLUME (PLASTICS RESINS AND RAW MATERIALS)

(all figures are in millions, except "unit cost")

	Total Pounds	Dollar unit, cost per lb.	Dollar value
Chemical Cotton Pulp	24·6	0·09	2·21
Nitric Acid	40·9	0·0566	2·32
Sulphuric Acid	19·6	0·0164	0·32
			4·85
ETHYL CELLULOSE	3·9	0·41	1·60
Chemical Cotton Pulp	41·2	0·09	3·71
Ethylene Dichloride	11·0	0·17	1·87
Caustic Soda	3·9	0·02	0·08
			5·66
CELLULOSE ACETATE AND C.A.B. (cellulose acetate butyrate)	60·2	0·58	34·92
Cellulose Acetate and C.A.B. Flake	279·4	0·36	100·58
Chemical Cotton Pulp	84·0	0·09	7·56
Acetic Anhydride	423·6	0·11	46·60
			154·74
Melamine Urea Resins	123·6	0·364	44·99
Methanol	57·5	0·05	2·88
Formaldehyde	115·0	0·04	4·60
Urea	45·4	0·0375	1·70
Melamine	7·2	0·45	3·24
			12·42
CELLULOSE VISCOSE	79·4	0·45	35·73
Chemical Cotton Pulp	95·2	0·09	8·57
Caustic Soda	102·1	0·02	2·22
Carbon Disulphide	27·8	0·05	1·39
Sulphuric Acid	143·0	0·0164	2·35
Glucose	39·7	0·0375	1·49
			16·02

the question of raw materials even more important. It seems certain that the coal industry, which has been the mainstay of plastics production in the past, would in any event be insufficient to meet future requirements. Consequently, the arrival of petroleum and agricultural products as additional sources are likely to remove unnecessary anxiety on this point.

Plastics having been put forward as excellent substitute materials for metals and other things in short supply, it seems probable that a large proportion of the applications will in the future continue to be filled by plastics. Consideration of American production of plastics over a number of years gives some indication of the great rate of growth of the industry.

A comparable expansion has occurred in other countries, notably in Germany and in Great Britain.

From the raw material point of view, the plastics industry must be considered in relation to the other closely related industries, notably the chemical industry, the rayon industry, and the synthetic rubber industry, all of which are interested in similar raw materials. The synthetic rubber industry in particular is likely to have enormous repercussions owing to the large scale on which it is being carried out. The manifold by-products come mostly into the plastics field.

The statistics published in the United States, when war-time controls made precise figures available, give the clearest picture of the relationship between chemicals and the plastics obtained from them.

For a consideration of the raw materials it is advisable to examine the main individual sources. These can be taken as coal derivatives, petroleum derivatives, agricultural derivatives, and cellulose.

Coal as a Plastics Raw Material. For many years coal has been the outstanding raw material in the production of chemicals employed for most synthetic resins and plastics. Coal is freely available in large quantities in the United States, Great Britain, Germany, and Russia, being the source of many chemicals. At the present time it is still unchallenged in the production of polyamides and phenolic resins. In some other cases petroleum and agricultural materials are beginning to exert a strong competitive action.

In its normal industrial handling, coal is converted into a number of materials, the most important being light oil, coal-tar, coke and water gas. All of these are concerned with the production of plastics of one sort or another. The main ingredients which are derived from coal-tar and light oil, are benzene, naphthalene, tar acids, and coumarone resin fractions.

A little styrene is also obtained.

Enormous quantities of synthetic resins have been produced from these materials. Phenolic resins are made by the reaction between phenol or the homologues such as cresol, xylenol, etc. (also obtained from coal-tar) with an aldehyde. The use of cresols and xylenols came in only during the four-year war. In most countries, the demands for phenol has outstripped the amounts which can be manufactured by refining coal-tar distillates. As a consequence, synthetic phenol production is already widely established. It is still substantially a coal activity, for the starting material is again a coal derivative in the form of benzene.

TABLE 12

SOME COAL REQUIREMENTS FOR PLASTICS (WAKEMAN AND WEIL)[35]

PHENOLIC RESINS, 1941	
Total Phenolic Resins	157,000,000 lb.
Based on Phenol	99,000,000 lb.
Based on Cresol, Xylenol, etc.	68,000,000 lb.
Phenol	96,000,000 lb.
Cresols, Xylenols, etc.	36,000,000 lb.
Coal required for phenol products	68,000,000 tons*
Tar acids for other type	57,000,000 tons*
NYLON PRODUCTION, 1941	
Production	8,000,000 lb.
Adipic Acid	5,000,000 lb.
Hexamethylene Diamine	4,000,000 lb.
Coal required (via Phenol)	6,800,000 tons
POLYSTYRENE, 1941	
Production	5,000,000 lb.
Coal required (via Benzene)	1,600,000 tons
ALKYD RESINS	
Phthalic Anhydride used	60,000,000 lb.
Naphthalene required	55,000,000 lb.
Coal required	24,000,000 tons

* Not additive.

In the United States in 1947 the production of plastics provided the greatest outlet for phenol, representing more than 60 per cent of production. In the United States at the present time only a fraction is derived from coal-tar refining, while the remainder is made synthetically.

In 1947 about 30 million pounds phenol came from 625 million gallons of coal-tar. In 1947 240 million pounds synthetic phenol was made, involving 35·5 million gallons of benzene. Of this about 15 per cent is made by the Raschig process, the remainder being made by other synthetic methods. There are indications that some of these materials may in due course be derived from petroleum sources, especially as the processes for aromaticisation of petroleum develop.

TABLE 13

MAXIMUM POSSIBLE CHEMICAL PRODUCTS FROM COAL CARBONISED IN U.K. AND U.S.A.[30]

	Coke ovens		Gas works		U.S.A.
	Yield	Tons	Yield	Tons	Tons
Coal	1 ton	22,000,000	1 ton	18,000,000	78,000,000
Coke	12 cwt.	13,000,000	10 cwt.	9,000,000	47,000,000
Tar	8·5 gal.	1,000,000	11 gal.	1,000,000	3,600,000
Crude benzole	3·6 gal.	300,000	3 gal.	200,000	1,100,000
Gas	40 therms	2,500,000	75 therms	3,500,000	1,100,000
	Per cent		Per cent		
Methane*	28	700,000	20	700,000	2,500,000
Benzene†	60	180,000	50	100,000	650,000§
Toluene†	15	45,000	12	24,000	130,000§
Styrene†	1	3,000	0·5	1,000	11,000
Indene†	2·5	7,500	1	2,000	27,000
Naphthalene‡	7	70,000	1	10,000	100,000§
Tar acids‡	2	20,000	4·5	45,000	140,000§

* Percentage based on gas yield.
† Percentage based on crude benzole yield.
‡ Percentage based on crude tar.
§ Figures based on actual recorded production.

Phenolic resins are employed in many forms of production. They are used for moulding powders, casting resins, coating materials, laminated products, and so on. There is every indication that their use may continue to expand, especially with the arrival of injection moulding, and their use as adhesives in the plywood industry.

It seems definite that the polyamide resins, i.e. nylon, are destined for very large-scale production. As things are at present, so far as raw materials are concerned, they are completely dependent on supplies of phenol. The chief chemicals employed—adipic acid and hexamethylene diamine, both come from phenol. According to Wakeman and Weil, 8 million pounds of nylon was made in 1941, requiring 5 million pounds of adipic acid, and 4 million pounds of hexamethylene diamine. Already in 1947 nylon required 125 million pounds of phenol and in 1948 almost 180 million pounds. Already difficulties in the

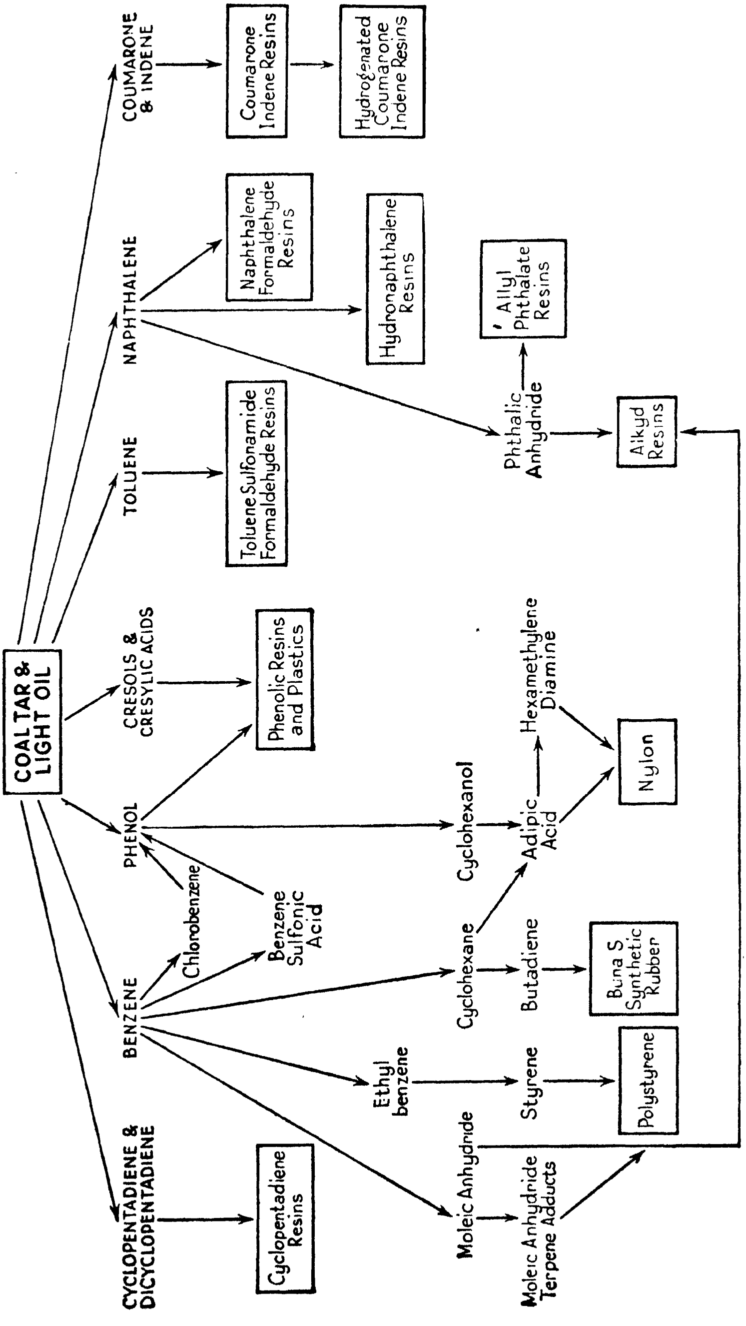


Fig. 16. Plastics from coal-tar

supply of phenol have led to alternate processes for the production of adipic acid. Even these are based on benzene, another coal-tar derivative.

Benzene is, of course, a parent chemical for numerous other plastics, which are of great importance. A leading example is polystyrene. Small quantities of styrene are obtained in the refining of coal-tar products, and these are converted into polystyrene. However, large-scale production at the present time is dependent on synthetic methods. These are based on ethyl benzene, which is produced from benzene and ethylene.

TABLE 14

REPRESENTATIVE YIELDS FROM THE DISTILLATION OF COAL TAR IN THE U.S.[25]

Distillates	Percentage by Weight of Dry Tar
Naphthalenes	20·9
Phenol and Phenol homologs	2·2
Xylenes, cumenes, and isomers	1·1
Coumarone, indene, etc.	0·6
Crude benzene and toluene	0·3
Sub-total	25·1
Miscellaneous	30·2
Pitch (460° F. melting-point)	44·7
Grand Total	100·0

In 1941 5 million pounds weight of polystyrene was produced. In 1947 production was 90 million pounds. In Germany up to 1944 production had for some time been of the order of 50 million pounds. However, these figures are completely overshadowed by the 250 million pounds per annum of styrene produced at the peak of the American synthetic rubber programme. This involved the production of styrene from every conceivable raw material, and placed great strain on the supply of benzene. This synthetic rubber programme has had a great influence on the development of polystyrene as a plastic. No other industrial development has a comparable influence on any other synthetic product. In the case of benzene the latest available figures emphasise its paramount importance. In 1947 out of a production of 1·2 billion pounds, phenol required 235 million pounds, styrene took 280 million pounds, while nylon required 125 million pounds.

Already, with the slackening off in the synthetic rubber production, styrene is being made available to the plastics industry at remarkably low cost (13 cents per lb.).

It should be remembered, too, that phenol and cresol are consumed in quite large quantities in the production of the plasticisers which are so widely used for thermoplastics and cellulose plastics, notably tricresyl phosphate, triphenyl phosphate, etc. Latterly shortages of intermediates have led to a reduction in output of plasticisers. The output of plasticisers in 1939 was 29,870,000 lb.

TABLE 15

UNITED STATES PRODUCTION OF PLASTICISERS[34]

Chemical	Production 1,000 lb. 1944	Production 1,000 lb. 1946
Grand Total	169,269	114,596
PLASTICISERS, CYCLIC. Total	138,955	83,839
Phosphoric acid esters: tricresyl phosphate	13,552	10,348
Phthalic acid or anhydride esters. Total	98,945	57,925
Dibutyl phthalate	45,915	12,643
Diethyl phthalate	9,700	10,710
Dimethyl phthalate	18,882	5,469
All other	24,508	23,520
All other cyclic plasticisers	26,458	15,566
All others	24,508	23,520
PLASTICISERS, ACYCLIC. Total	30,134	30,757
Azelaic acid esters	37	34
Citric acid esters: triethyl citrate	539	
Lauric acid esters	364	367
Oleic acid esters	3,148	4,379
Phosphoric acid esters	2,160	1,381
Sebacid acid esters: dibutyl sebacate	5,853	2,335
Stearic acid esters. Total	3,074	5,881
Butyl stearate	832	1,469
Glyceryl monostearate	1,061	2,088
All other	1,181	2,120
All other acyclic plasticisers	15,139	16,344

Alkyd Resins. Another leading coal-tar product, naphthalene, is almost as important as phenol and benzene as a raw material. For the production of alkyd or glyptal resins is almost as large as the production of phenolic resins. This consumption has grown from almost negligible dimensions since 1925. Yet in 1941 the amount made in the United States reached 128 million pounds based on phthalic anhydride, and 9½ million pounds based on maleic anhydride with naphthalene as the other component. These are produced by oxidation of phenol and benzene respectively. In 1941 60 million pounds of phthalic anhydride were used, derived from 55 million pounds of naphthalene, in turn obtained from 24 million tons of coal. In 1947 the alkyd resin output was 283 million pounds.

In 1945 260 million pounds of naphthalene were obtained, of which 170 million was converted into phthalic anhydride.

The staggering increases in demands for these materials, which are also very widely used for plasticisers, has led to notable shortages of naphthalene. These shortages cannot be met in present conditions and further expansion is limited by this factor. Once again there are distinct possibilities that naphthalene will be produced from petroleum products by aromaticisation processes. The production of phthalic anhydride from o-xylene derived from petroleum is already well advanced.[32]

Water Gas as a Source of Plastics. Water gas is obtained mainly by passing steam over coke. It is a most important source of formaldehyde which is a primary essential raw material for the plastics industry. Thus coal serves not only as the main source of phenol, cresylic acid and synthetic phenol, but also as the main source of the other chief constituents of thermosetting resins.

Formaldehyde is made in limited amounts by direct oxidation of natural gas. It is produced mainly, however, by oxidation of synthetic methyl alcohol, which is produced from water gas. A proportion of methyl alcohol is obtained from water gas derived from methane. In 1945, in the United States, total formaldehyde production was of the order of 485 million pounds, while in 1947 it exceeded 600 million pounds. About 243 million pounds was consumed in resins.

Formaldehyde is important in a number of other plastics activities. For example, it is used to harden casein plastic. A similar application is the conversion of casein into artificial wool, which is a large-scale production in the United States. Formaldehyde features in the newer melamine resins. It is used in the production of polyvinyl formal resin, a material which is acquiring great importance for coating and electrical purposes.

Besides formaldehyde, methyl alcohol is used in the production of other materials which go to the manufacture of plastics. By high pressure reaction with carbon dioxide, methyl alcohol yields acetic acid employed on a large scale in the manufacture of cellulose acetate. Carbon monoxide from water gas may be converted into a formate employed on a large scale in the manufacture of cellulose acetate.

Carbon monoxide from water gas may be converted into a formate which, with ammonia, yields formamide. This is dehydrated to hydrogen cyanide used to produce acetone cyanohydrin, which is then converted to methyl methacrylate. The use of this when polymerised to synthetic resin is increasing very rapidly.

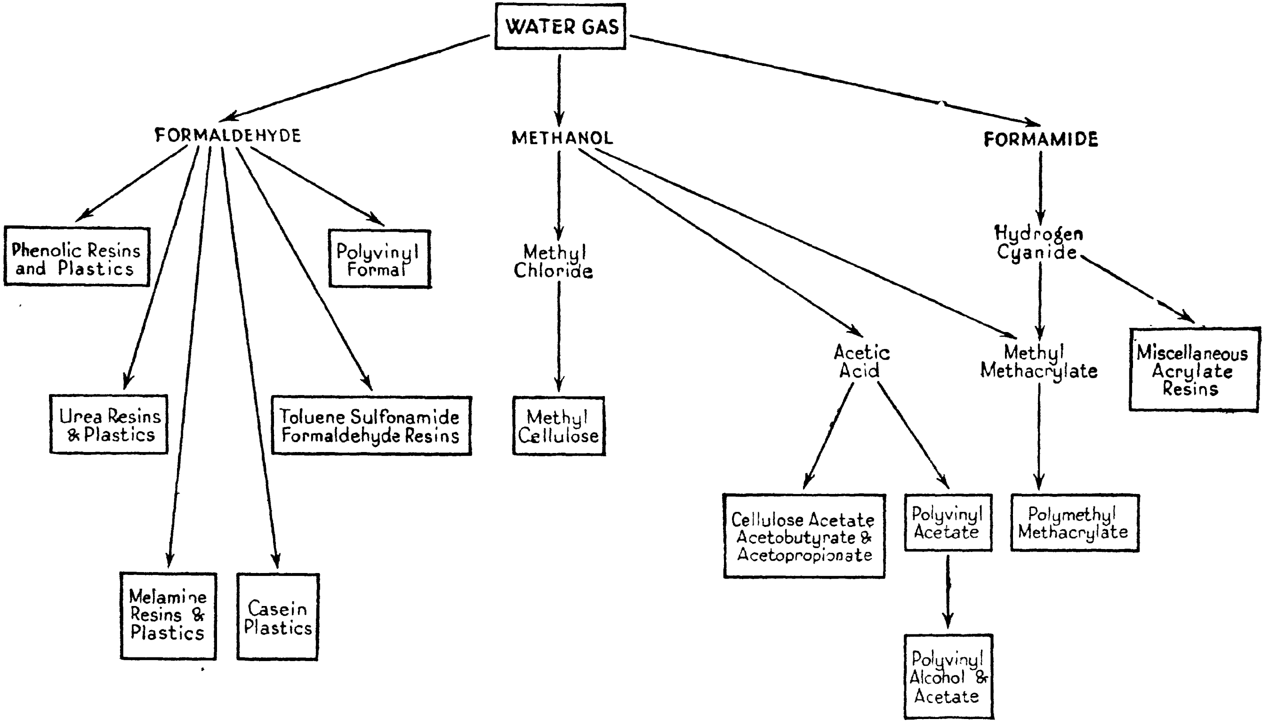


Fig. 17. Plastics from water gas

Coke itself serves directly as a source material for a very large number of synthetic organic chemicals, which are of primary importance to the plastics industry. Coke is converted by heating with limestone in an electric furnace into calcium carbide. This in turn provides acetylene and calcium cyanamide. Cyanamide is a leading material in the production of acrylic nitrile. This is employed on an increasing scale to produce oil-resisting synthetic rubbers, such as Perbunan and Hycar.

Calcium cyanamide is the chief source of dicyandiamide which may be converted into melamine. Melamine reacts with formaldehyde to give the melamine resins. These have already attained great importance which is steadily increasing.

Acetylene—A Basis of Present-day Plastics. At the present time acetylene obtained from calcium carbide is the chief source of ethenoid resins, butadiene, chloroprene and accessory chemicals for plastics. Acetylene is also obtained in large quantities from coal hydrogenation, petroleum wastes, etc. It is one of the most important industrial chemical raw materials. Until recently it has been neglected in this country.

For many years the Germans have concentrated on the use of carbide as a source of numerous chemicals, notably acetaldehyde, acetic acid, and numerous other derivatives. It is one of the mainstays of their chemical industry. It is certainly the backbone of their plastics industry and their synthetic rubber industry. Prior to the war they were consuming 600,000 tons per year. At the peak of their production in 1944 they produced at the rate of 1,320,000 tons per annum. Before the war Great Britain normally imported about 60,000 tons per year. British production of carbide was 3,100 tons in 1941, but 85,500 tons in 1946.

Among leading important industrial materials obtained from acetylene and having an important influence on plastics activities are:

Acetic acid, which is important for so many chemical industries including rayon, plastics, dyestuffs, explosives, etc.

Ethyl alcohol, which is necessary as a solvent for dyestuffs, chemicals, explosives, motor fuels, etc.

Acetone, which is essential for explosives, for lacquers, and innumerable chemical processes.

Ethyl acetate, which is a leading solvent.

Trichlorethylene; and a host of other synthetic chemicals, plasticisers, solvents, etc.

Acetaldehyde is easily converted almost quantitatively into acetic acid. Vinyl acetate is made by passing acetylene into a solution of

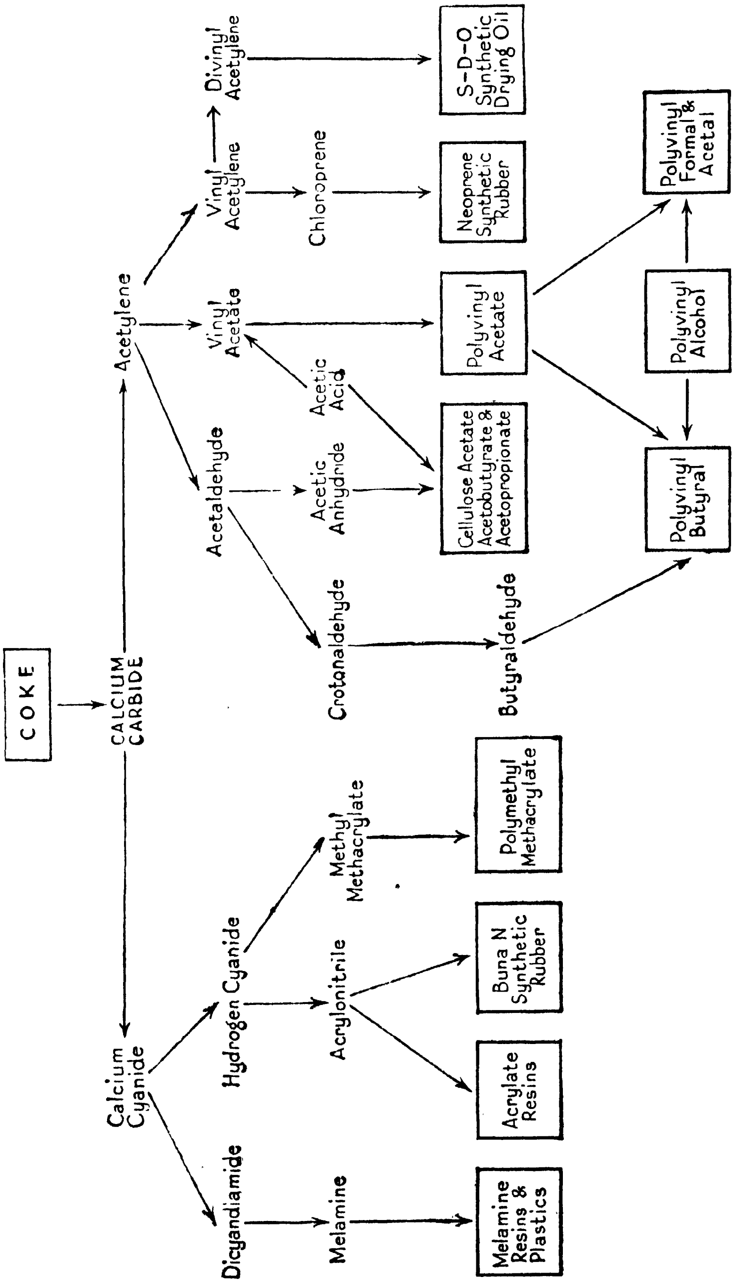


Fig. 18. Plastics from coke

acetic acid containing catalysts. Synthetic glacial acetic acid is being

$$CH \equiv CH + H_2O \rightarrow CH_3CHO$$

produced in immense quantities for the manufacture of cellulose acetate rayon, plastics, dopes, and films. It is used to make cellulose mixed esters such as cellulose acetobutyrate; it goes into the manufacture of polyvinyl acetate. These are quite apart from its important applications as a solvent and as a source of other valuable solvents and plasticisers.

Large quantities of acetic anhydride are also required by the acetate rayon and plastics industry. It is derived from acetic acid. In 1945 about 293 million pounds of acetic acid and 526 million pounds acetic anhydride were produced in the U.S. Catalytic processes of production have streamlined the manufacture. Several different processes are in commercial operation. The leading form of production is that based on the catalytic dehydration of acetic acid vapour. The use of a catalyst in the presence of a diluent make it possible to obtain acetic anhydride directly by oxidation of acetaldehyde. A plant with a monthly capacity of over one million pounds of such a process is in operation in Canada.[25] In the United States, a pyrolytic process for obtaining acetic anhydride from the acid has recently been put into operation.[21]

Acetylene is the parent material of numerous leading plastics, including the leading ethenoid resins such as polyvinyl chloride, polyvinyl acetate, etc. It is a source of vinyl acetylene, from which chloroprene is made, and of other polymers which have attained commercial significance. It is also the source of acetylene black, one of the leading filling materials in a number of industries, including rubber.

The importance of the carbide industry to plastics and industry in general has often been stressed. A brief discussion of the subject may not be out of place here.

The Manufacture of Calcium Carbide. The commercial manufacture of calcium carbide was started towards the end of the last century, and is now the largest consumer of energy in the electric furnace industry. The chief considerations in establishing a carbide factory are supplies of raw material which consist of limestone and coke or anthracite, and an abundant supply of cheap electric power.[5] The latter item contributes the chief cost factor. It is found that many large carbide factories have been set up on sites where cheap hydroelectric power is available. The preparation of raw materials is a matter of some importance owing to the high temperatures involved. Limestone, which is calcium carbonate, is heated at a very high temperature in lime-kilns to drive off carbon dioxide. The present-day practice employs lumps of lime reduced to pieces from 1 to 2 inches in size, while coal is reduced to pieces between ¼ and ½ inch mesh. The ingredients are mixed in proportions of about 100 parts of lime to 65 parts coal. The electric furnaces used are of special construction and have to withstand temperatures up to 3,000° C. Enormous electrodes are employed, ranging up to sizes of about 22 inches square. It is said that the progress in the design of electric furnaces for high temperatures follows developments in carbide manufacture.

As a result, manufacturing plants are chiefly located where there is unlimited water power. Norway and Sweden have been the chief European producers, although requiring to import coal. Until the war Great Britain was almost the only industrial country without a carbide industry, although possessing all the conditions necessary. The advances in the production of thermoplastics have largely come about because of this extensive manufacture. Correspondingly, the absence of such activity has led to neglect of the newer plastics, as in Britain.

In 1942 German carbide capacity was 1,320,000 tons per annum. Something over half this quantity was applied to "acetylene chemistry."

The actual production of carbide involves heating a mixture of lime and coal in electric furnaces by means of the electric arc. Extremely high currents are passed through built-up electrodes, Söderberg continuous electrodes appear to be generally used now in all parts of the world. This is a light steel casing containing a carbon paste. This is fed continuously into the furnace at the rate of 40 cm. per 24 hours. One typical modern plant, for example, using 23,000 kilowatts and a single three-phase supply three-phase 50 cycles with 180 volts across electrodes. The temperature reaches 3,000° C., when a fluid melt of carbide is formed and may be tapped off. The batch size is of the order of four tons in the most efficient plant, the furnace being continually fed with fresh materials. The largest commercial units produce about 200 tons per day. One ton of carbide requires 3,300 units of current for its manufacture, including the amount required for crushing, grinding, and all other processes.

Large capacity carbide plants are features of the enormous German synthetic rubber-manufacturing units.

The following account by Ambros[2] of the process carried out at the enormous Schkopau Buna Works gives some idea of the principles adopted.

Acetylene Production. "Carbide is manufactured at a large carbide works. The notable things about this factory, which has the most modern carbide furnace in the world, includes the amazing freedom from dust, which is carried away by a very comprehensive and efficient equipment. Another noticeable feature is the great extent to which mechanising and automatic control of the various furnace processes has been carried. The furnaces are fitted with external instruments which control all measuring, mixing, and regulating equipment, all of which are simultaneously co-ordinated, being supervised by specially skilled operatives. For example, the movement of the electrodes, the addition of coke and lime, etc., are all adjusted by these external controls. The mighty furnaces work continuously, the power being obtained from mid-German brown coal; the resulting carbide comes to the ovens as a molten white fluid, and enters a sealed water-cooled inclined conveyor, on which it cools down, and in so doing breaks into small pieces, so that at the end of the run cooled and crushed carbide is obtained.

"This carbide is ground to powder in a separate mill, and then goes to the gassing chamber, which works so that gassing is carried out without the formation of sludge, as a result of which dry, finely-powdered lime remains. This gassing chamber is also full mechanised, being operated by a few skilled men with the help of centralised controls. The remaining spent lime is partly used for agricultural purposes, while part is regenerated by burning and is used once again in the furnace. In this manner it has become possible to utilise a considerable portion of reclaimed lime in the manufacturing process."

The major production is, of course, butadiene, for synthetic rubber. Acetylene is obtained from carbide by addition of water. For the manufacture of butadiene the next step is to produce acetaldehyde. The manufacture of acetaldehyde from acetylene is carried out by passing acetylene into a dilute sulphuric acid solution containing a catalyst generally composed of mercury salts. This is one of the fundamental reactions of industrial chemistry. This is the basis of the major portion of Germany's large-scale production of Buna synthetic rubbers.

Apart from the carbide process, the Germans produced about 5,000 tons per month of acetylene by the electric arc process at Hüls. There were three sources of raw material:

(*a*) Natural gas, mainly composed of methane.
(*b*) Coke-oven gas which had passed through a deep refrigeration system—the Linde process.
(*c*) Refinery gases.

The gas is passed into an electric arc formed by 6,000-volt A.C. 50-cycle current converted in a mercury rectifier to 7,000 volts D.C. at 7,000 kilowatts. Each arc uses 7,000 kilowatts and produces 4,200 cubic metres per hour product. Power consumption is about 4 kWh. per lb. crude acetylene and about 5 kWh. per lb. pure acetylene.

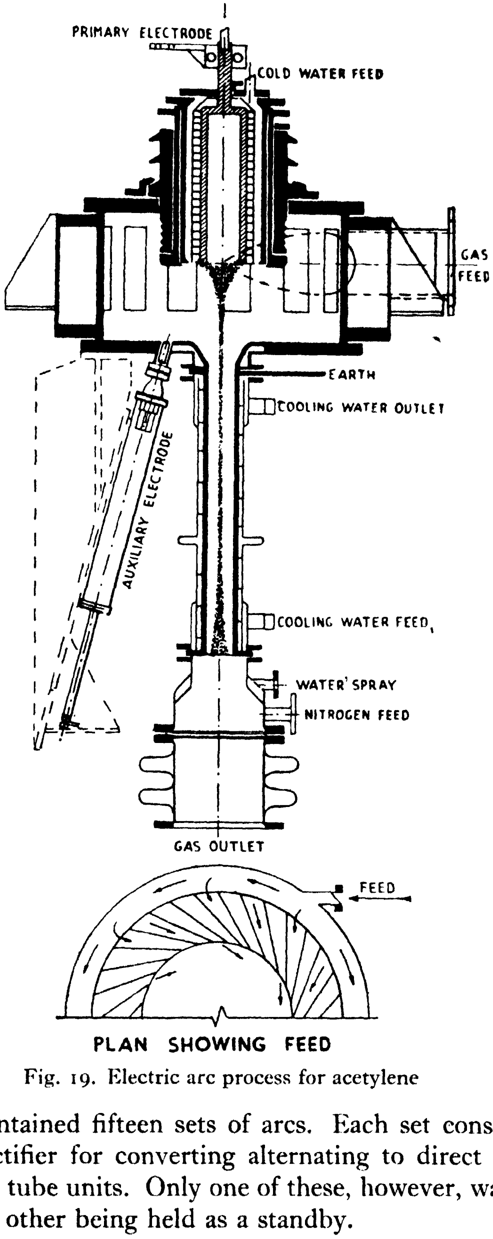


Fig. 19. Electric arc process for acetylene

The plant contained fifteen sets of arcs. Each set consisted of one mercury arc rectifier for converting alternating to direct current and two arc-reaction tube units. Only one of these, however, was on stream at any time, the other being held as a standby.

The arc operated at 1·5 atmos., 1,000-volt direct current, a reaction tube terminal temperature of 1,600° C. being reached; 7,000 kilowatts were required for a gas input of 2,800 cubic metres per hour. The conversion per pass was 50 per cent and the ultimate yield was acetylene 45 per cent, carbon black 5 to 6 per cent, and from 2 to 10 per cent of ethylene, depending on conditions. The production per arc was approximately 15 tons of acetylene a day.

The arc reaction tube unit used is shown in the figure. The high voltage lead to the primary electrode, which was made of copper, entered at the top. The electrode was jacketed for water-cooling and insulated with porcelain.

The feed gases entered tangentially, circulating round in a circular space in the expanded head section and passed through vertical slots to the arc zone at the centre and then down to the reaction tube. This produced a high velocity swirling action and so prevented the electrode burning out or carbon disposition. The second electrode consisted of a copper gasket at the head of the reaction tube, and was earthed. An auxiliary electrode was used for starting up.

After quenching the exit gas from the reaction tube to 150° C. (dew point 92°), it was then passed through two cyclones in which from 60 to 70 per cent of the total carbon black present was deposited. The gas was sprayed with water in a wash tower and passed through bag filters to remove the residual black, the bags being heated to prevent condensation. The gas was then sprayed with water at 20 to 25° C. to bring the temperature of the gas below the dew-point and so deposit most of the water carried in the gas.

After removing the higher boiling constituents by counter-current washing in an aliphatic oil, the gas was compressed to 19 atmospheres and absorbed in water in perforated plate towers. The acetylene was then stripped from the water by four stage flushings to a final pressure of 0·05 atmospheres absolute.

The gas obtained from the first stage was too low in acetylene (45 per cent), and this was therefore recompressed and recycled through the absorber. The gas from the second, third, and fourth flushes, however, was brought together as crude acetylene of 90 per cent purity. It was brought up to 97 per cent concentration by (i) low-temperature condensation and evaporation, using liquid ammonia, and (ii) scrubbing with a petroleum distillate which removed the higher acetylenes. Carbon dioxide was then removed by scrubbing with caustic soda solution to give a final purity of 97 to 98 per cent.

Oxidation of acetaldehyde yields acetic acid. Vinyl acetate is made by passing acetylene into a solution of acetic acid containing catalysts.

The United States is a large producer of calcium carbide. As a result, the firms concerned have played a leading part in developing thermoplastics of the vinyl type. For example, the Carbide and Carbon Corporation, specialising in carbide production was responsible for the first large-scale commercial production of polyvinyl chloride and its copolymers in the form of Vinylite products. In a similar manner Shawinigan Corporation in Canada has been largely responsible for the development of products such as polyvinyl acetates, alcohols, formals, acetals, etc.

B. F. Goodrich Co. have a very large plant at Niagara, where the variety of polyvinyl chloride known as Geon is prepared.

It is interesting to note that the United States firms would not launch out into synthetic rubber production on an acetylene basis. With all their resources of lime and coal and unlimited cheap electrical power, they held back. There is much evidence to show that they were, nevertheless, extremely interested in the possibility, being cautious merely because of the developments with petroleum products which they knew lay ahead.

It is evident that acetylene can easily be converted into ethylene by hydrogenation. Ethylene is the basis of numerous important plastics. It is also prepared by dehydration of ethyl alcohol which is easily obtained from acetylene via acetaldehyde. Ethylene is also available in vast quantities in coke-oven gases although this source has not yet been exploited as a source of plastics.

Acetone is of outstanding importance in plastics activities in every sense—i.e. as a raw material, as a solvent, and as a chemical intermediate. Although obtained from a number of sources, one of the chief is from acetylene. It is made by direct action of acetylene and steam. Acetylene and a large excess of steam is passed over a zinc oxide—iron oxide catalyst—contained in reaction tubes maintained at constant high temperature by means of molten salt. It can be obtained indirectly from acetylene by first making acetic acid. This is then passed over heated lime. Acetone is a parent material in the production of methyl methacrylate resins.

Reppe Chemistry.[40] The Germans have devoted a tremendous amount of attention to the possibilities of acetylene. The work of Reppe has overshadowed all other work in this field. So much so that acetylene chemistry is known as "Reppe Chemistry".

The production of vinyl chloride and vinyl acetate by combining acetylene with hydrochloric and acetic acids respectively is well known. Reppe has extended this process to a wide range of alcohols, thioalcohols, amines and carboxylates, and has shown that the reaction is quite general. In the presence of alkaline catalysts acetylene is introduced between hydrogen and oxygen, sulphur, nitrogen or COO′ whereby vinyl ethers, sulphides, amines, and esters are produced. Thus to make vinyl methyl ether, acetylene is bubbled through methyl alcohol at 160°–200° in the presence of 1%–2% of potassium alcoholate, the pressure being maintained high enough to prevent boiling.

$$CH_3OH + CH{\equiv}CH \longrightarrow \underset{\text{Vinyl methyl ether}}{CH_3O.CH{=}CH_2}$$

This material is of considerable interest since it can be hydrolised with water to yield acetaldehyde and methyl alcohol. This has advantages over the standard method. It also offers an alternative synthesis for butadiene and synthetic rubbers.

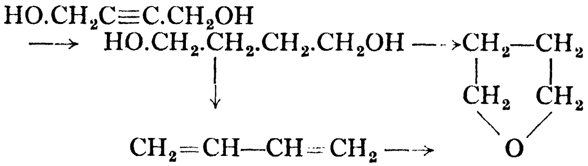
Returning to Reppe's acetylene chemistry, the next important type of reaction is that leading to the production of triple-linked "ethynyl" compounds. Here the most startling feature is the use of copper and silver acetylides as catalysts, these compounds having formerly been avoided because of their explosive properties. The interaction of acetylene and formaldehyde indicates how the method provides important intermediates.

$$CH_2O + CH{\equiv}CH \longrightarrow \underset{\text{propargyl alcohol}}{CH{\equiv}C.CH_2OH}$$

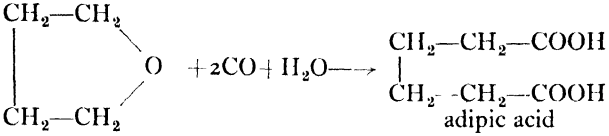
$$2CH_2O + CH{\equiv}CH \longrightarrow \underset{\text{butyne diol}}{HO.CH_2C{\equiv}C.CH_2OH}$$

Similar reactions occur with ketones, e.g. acetone, and with certain amines, e.g. dialkylamines, whereby triply unsaturated compounds result.

Butyne diol is clearly an extremely important intermediate, and was made on a large scale at Ludwigshaven. It can readily be hydrogenated to yield 1 : 4 butylene glycol, which in turn can be converted by dehydration to butadiene (for synthetic rubbers) either directly or through tetrahydrofurane.



Tetrahydrofurane is a valuable solvent, particularly for P.V.C., but in addition to this it can be reacted with carbon monoxide and water to give adipic acid. In this way, a new route is provided for nylon production.



Propargyl alcohol is a useful starting point for allyl alcohol, n-propanol and propionaldehyde, or it may be dimerised in the presence of oxygen and cupric chloride to give hexadiynol.

$$\underset{}{CH{\equiv}C.CH_2OH} \longrightarrow \underset{\text{allyl alcohol}}{CH_2{=}CH.CH_2OH} \longrightarrow \underset{\text{n-propanol}}{CH_3.CH_2.CH_2OH}$$

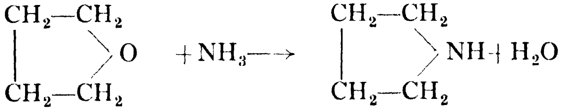
$$2CH{\equiv}C.CH_2OH \longrightarrow \underset{\text{hexadiynol}}{HO.CH_2C{\equiv}C{-}C{\equiv}C.CH_2OH}$$

Hexadiynol can, through hexanediol, lead to caprolactam, an interesting intermediate in the production of modified polyesteramides.

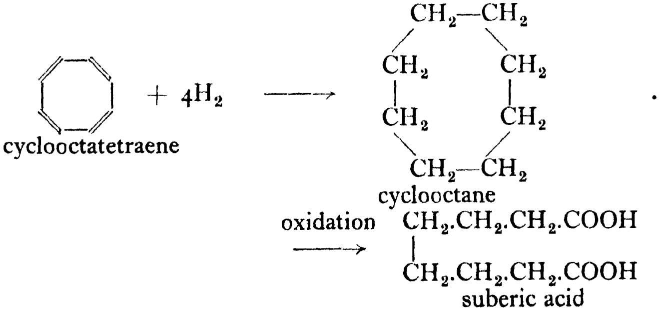
Space forbids full details of all the possibilities opened up. Obviously the changes can be rung indefinitely by employing other aldehydes, e.g. acetaldehyde, amines, ketones, etc. Polyhydroxy compounds have evident value in alkyd resin production, etc., and in polyurethane syntheses. Reppe has found a simple route to acrylates through the interaction of acetylene, carbon monoxide and water, thus:

$$CH{\equiv}CH + CO + H_2O \longrightarrow CH_2{=}CH.COOH$$

If water is replaced by alcohols, then esters result. Furthermore, he has produced pyridines and pyrrolidine derivatives by the action of ammonia or amines on tetrahydrofurane.



One further point is the discovery that acetylene, when polymerised, need not necessarily follow the Nieuwland reaction leading to vinyl



acetylenes. It can under suitable conditions give an eight membered ring, cyclooctatetraene. Apart from providing a simple general route to an industrially novel set of compounds cyclooctatetraene can be used specifically, through hydrogenation and oxidation, as a method for preparing suberic acid.

RAW MATERIALS—PETROLEUM

Oil as a Source of Synthetics. The immediate future of plastics is closely connected with petroleum. It is of interest to note that in 1941 the plastics industry consumed intermediates which required as raw materials some 700 million cubic feet of natural gas for methane, 2·9 billion cubic feet of propane and ethylene, 270 million cubic feet of propane-butane mixtures, 70 million cubic feet of propylene, and 150,000 barrels of petroleum. Enormous quantities are used in the production of synthetic rubber. This is due to the fact that the necessary raw materials may be obtained from this source at a remarkably low cost. The United States, as the world's greatest oil producer, is obviously favourably placed in this respect. This position may change as American resources become exhausted. Other countries which have large supplies of oil available are shown in Table 16.

Tugendhat[33] has stated in relation to a possible British refining industry with a capacity of 5,000,000 tons per year that: "in addition to over 4,000,000 tons of liquid and solid products there would be between 240,000 and 500,000 tons of gases. Without dehydrogenation or aromatisation the yields of unsaturates, mainly ethylene, propylene and butylenes, could be between 120,000 and 200,000 tons. These yields would be considerably increased by dehydrogenation. By a new aromatisation process which has been developed in Britain, using naphtha or gas oil as starting material, it would be possible to produce from each 100,000 tons feeding stock approximately 25,000 tons of unsaturated gases, ranging from ethylene to butylenes, 30,000 tons of low and medium boiling pure aromatic liquids, such as benzol, toluene, xylene, naphthalenes, etc., the remainder being methane and ethane and a small fraction of heavy tar and coke.

Looking at these materials from the point of view of the plastics industry, I may say that it would be possible to produce many tens of tons of thickol, polyvinyl chloride, styrene, methacrylates, glycols, glyptal resins, benzol for phenols, etc., not forgetting butadiene, acetone, acetic anhydride and a goodly number of various solvents, plasticisers, varnish bases and drying agents."

Large scale production of chemicals from petroleum is already under way in Great Britain at four new plants.

TABLE 16

PERCENTAGE PRODUCTION OF PETROLEUM BY COUNTRIES, 1947

	Per cent
United States	63
Other countries (Russia, Mexico, South America, Iran, Iraq)	35·5
British Commonwealth	1·5

TABLE 17

WORLD CRUDE OIL PRODUCTION, 1947

	1,000 barrels
World Total	3,159,000
United States	1,988,100
Venezuela	435,100
U.S.S.R.	197,600
Iran	155,000
Saudi-Arabia	89,900
Mexico	56,500
Iraq	35,400
Roumania	28,900
Colombia	25,700
Argentina	21,900
Trinidad	20,500

It is unnecessary to stress the general importance of oil. As in the case of coal, its primary function is as a source of power. An ever-growing number of commercial materials have been obtained from coal via coal-tar for many years but a similar trend set in for petroleum derivatives. The potentialities as a source for synthetic resins and synthetic rubber, etc., add further to its importance.

Dunstan has admirably summarised the position:[11]

"Although, without doubt, the principal use of petroleum will always be as a source of fuel, lubricants and road-surfacing asphalt, chemical developments in recent years have opened up entirely new vistas of usefulness. The chemist views petroleum not only as a mixture of petrol, kerosene, etc., but as an assembly of carbon and hydrogen atoms put together by nature like so many bricks to form edifices of certain specific designs known as paraffins, naphthenes and aromatics. He realises, moreover, that it is possible to break down these structures which may be useful only as fuel, into their component bricks and with these bricks to reconstruct new edifices of a design and pattern suitable for quite different purposes. For example, by demolition of heptane, one of the hydrocarbons in petrol, and the regrouping of the carbon and hydrogen it contains, it is entirely possible to build toluene for explosives or styrene for flexible glass or butadiene for synthetic rubber.

By combining these derived hydrocarbons with oxygen there can be made alcohol, glycerol and acetaldehyde, the parent materials for the newest types of synthetic textiles, ornamental moulded plastics, resins, paints and varnishes, synthetic rubbers, flotation agents, insecticides and detergents. In effect, all the well-known products known of old as originating from coal-tar are obtainable from petroleum bricks."

As petroleum is a major source of olefines, notably ethylene, it is not surprising that the industry should become interested in the growing field of synthetic resins. But as Frölich[13] has pointed out, "Because of its general set-up, the petroleum industry is, as a rule, dependent upon a relatively large scale of operation to obtain the full advantage of its law potential manufacturing costs." So that unless some great industry is affected, progress cannot be very rapid. Obviously, synthetic rubber is a major field offering scope for such large-scale operations. Thus the activity with synthetic rubber is likely to bring in its trail the other profound developments with synthetic resins. Without it their progress would be greatly retarded.

Frölich has drawn up the following list of products connected with the general aspect of synthetic rubber which are either now being manufactured wholly or in part from petroleum products, or for which the petroleum industry would be able to supply raw materials.

1. Natural petroleum resins by light hydrocarbon precipitation.
2. Cracking-coil tar resins by condensation of highly condensed petroleum hydrocarbons, such as those which are present in the tar bottoms from the cracking operation, with formaldehyde or ethylene chloride.
3. "Santoresin" by reaction of olefines and diolefines in the presence of aluminium chloride.
4. Polystyrene by polymerisation of styrene, which may be produced from ethylbenzene made by alkylation of benzene with ethylene.
5. Polybutylene by polymerisation of unsaturated gaseous hydrocarbons to give substantially linear polymers ranging in consistency from that of a viscous oil to rubbery materials with molecular weights as high as 300,000.
6. "Buna" rubber and similar products by polymerisation of butadiene made from acetylene or from n-butylenes.

7. Neoprene rubber by polymerisation of chloroprene derived from acetylene.
8. "Thiokol" by condensation of sodium polysulphide with ethylene dichloride or other chlorine-containing derivatives.
9. Polysulphones by reaction of olefines with sulphur dioxide.
10. Vinyl resins by polymerisation of vinyl chloride and vinyl acetate derived from acetylene or ethylene.
11. Phenol-formaldehyde resins by condensation of formaldehyde with phenols.
12. Alkyd resins by reaction of dibasic acids with polyhydric alcohols —e.g. ethylene glycol and diethylene glycol, from ethylene, and glycerol which may be prepared from propylene.
13. Ethylcellulose by reaction of cellulose with ethyl chloride, or diethyl sulphate produced from ethylene.
14. Cellulose acetate by reaction of cellulose with acetic anhydride, which may be derived from ketene obtained by thermal decomposition of acetone produced by dehydrogenation of isopropyl alcohol.
15. Acrylate and methacrylate resins derived in various ways from olefinic compounds.

But particularly in regard to all these activities it has been shown time and time again that so many factors are changed when small-scale results are transferred to commercial unit operations that it is not safe to base commercial operations on small-scale results. This is another reason why full-scale operations with synthetic rubbers have profoundly influenced plastics.

Waste in the Oil Industry. The history of oil is probably the most outstanding example of waste. And nowadays whenever there are wastes there is an almost automatic implication of plastics. From the time of its discovery in the United States in 1859, oil was prized most highly because of its kerosene content, becoming the fuel for oil lamps. All the low boiling fractions were regarded as a dangerous nuisance and were dumped. The high boiling fractions were equally useless. The arrival of the internal combustion engine in due course completely changed this situation, so that kerosene became very much a secondary material. The once embarrassing fluid now acquired paramount importance as a motor fuel. To bring the matter into its right perspective it is estimated that manufacturing cost of petrol in the United States is about 3 to 4 cents per gallon, while to produce it from coal costs about four times this amount.

As the number of motor-driven vehicles expanded at a terrific rate, petrol production could not keep pace with the demand (incidentally, nor could rubber production). The direct distillation method of production was terribly wasteful and inefficient. A shortage appeared imminent. The first step forward came in 1912, when the Burton[8] process of cracking was introduced. Not only was this epoch-making as regards motor-spirit production, but it also marked the beginning of synthetic processes, catalytic methods, etc. With each improvement the amount of waste has decreased, and all sorts of by-products have appeared.

Composition of Petroleum. Petroleum consists of a mixture of hydrocarbons whose composition varies with place of origin. It may contain members of the paraffins, together with cyclo-paraffins and also aromatic hydrocarbons. Nearly always associated with petroleum are gaseous paraffins known generically as "natural gas." Straightforward rectification of petroleum yields:

Petrol or gasoline or motor spirit, up to 60° C., consisting of pentane and hexane.

Benzine distilling up to 90° C., made up largely of hexane and heptane.

Ligroïn distilling up to 120° C.

Kerosene boiling between 150° C. to 300° C.

Heavy oil distilling above 300° C. used for lubricating oils and petroleum jelly.

Tars, asphalts, etc.

Natural Gas. A great deal has been heard about "natural gas." Natural gas consists of a mixture of gaseous paraffins, chiefly methane, ethane, propane, butane and isopentane. Wherever petroleum is found there is generally a certain amount of natural gas about. However, the gas does occur frequently alone without any associated petroleum. There are many seemingly unlimited subterranean reservoirs which when tapped blow off in a spectacular manner. Enormous amounts are available in the United States and in the U.S.S.R. In the United States about 45 per cent comes from oil wells. For many years all natural gas was allowed to blow off to waste into the air.

This natural gas is expected to be a primary source of raw materials for synthetic resins and synthetic rubbers. In recent years a certain amount has been stripped for petrol. In the United States, for a number of years, a large proportion of natural gas has been used to perform the functions carried out by coal gas. There is a network of natural gas pipe-lines spreading all over the American continent. In other countries this activity is more localised.

In spite of these applications of natural gas, the major portion of available gas is still being wasted into the atmosphere. As raw material for any products it is there for the asking. It is not to be wondered that the petroleum concerns are interested in the possibilities which may lead to major uses. According to Grosse and Ipatieff,[16] there is available in the United States annually from all sources 300 billion cubic feet of ethane, 120 billion of propane, and 70 billion cubic feet of butanes.

TABLE 18

THE MAIN CONSTITUENTS OF NATURAL GAS[11]

	M.P. °C.	B.P. °C.
Methane	—182	—161
Ethane	—172	— 89
Propane	—187	— 42
n-Butane	—135	— 0·6
iso-Butane	—145	— 10
n-Pentane		— 37

The processes which lead to these products, which may form the basis for synthetic resins, are briefly as follows:

Cracking Processes with Oils. Cracking is a heat treatment which converts hydrocarbons of relatively high boiling points and high molecular weights into materials of lower boiling points and low molecular weights, suitable for use as motor spirit. It results in an increase in the amount of total motor spirit obtained from crude oils. These oils may be cracked under high pressure in the liquid form, or at higher temperatures as gases. Invariably large quantities of gaseous products are obtained, consisting mainly of olefines and some diolefines.

Cracking Processes with Gaseous Hydrocarbons, i.e. Natural Gas. Gaseous hydrocarbons are submitted to high temperatures when dehydrogenation occurs with the formation of olefines. The paraffins tend to produce simpler molecules of the corresponding olefine, sometimes lower paraffins and often hydrogen. Thus, with the exception of methane, the paraffins such as ethane, propane, n-butane, and isobutane, yield olefines such as ethylene, propylene, and four isomeric butylenes.

The decomposition takes hours at 400°C., but only seconds at 800°C. It is very profoundly influenced by catalysts, such as chromium oxide, molybdenum oxide, vanadium oxide, together with aluminia or magnesia, activated charcoal, zinc-chromium alloy, etc., all of which facilitate dehydrogenation at lower temperatures, about 350° C.

The following account by Grosse, Morrell and Mavity[17] clearly explains the position:

The dehydration of the paraffin gases of the corresponding olefines is the problem of fundamental importance to the oil industry. The technical problem of efficiently converting gaseous olefines into liquid motor fuel has been solved within recent years by both catalytic and purely thermal processes. Therefore, a process for the conversion of paraffins into olefines would put to good use all the paraffin gases except methane. These gases are available in enormous quantities from such sources as natural gas, and gasoline, petroleum, petroleum gas, gas from the cracking processes, coke-oven gas, and refinery gasoline.

A catalytic dehydration process has been developed for converting normal and isobutane, propane, butane and ethane to the corresponding olefines. Briefly the process consists in passing the pre-heated gases over a suitable catalyst. The outgoing gases contain olefine and hydrogen besides the unreacted original paraffins. The olefines are polymerised or used in alkylation. The hydrogen is separated and the unreacted original paraffins are recycled.

The plant consists essentially of a furnace, banks of catalyst reactors, and hydrogen separation units. Automatic controls alternate the flow of paraffin gases first through the furnace and one section of reactors, and then through another, while the catalyst is being regenerated in the first section. The regeneration consists in passing automatic control amounts to air mixed with composition gases or steam to burn off the carbon on the catalyst at a moderate composition temperature, usually below 900° C. A feature of the process is that the length of operating cycle is short, usually of the order of one hour. The advantages of the catalytic process over purely thermal cracking are the much larger overall yields of the corresponding olefines and a much higher reaction velocity.

According to Frey and Hepp[12] the reactions which occur and the yields which are obtained under different conditions are illustrated in Table 19.

Conversion of Paraffins to Olefines. In fact, the paraffins, with the exception of methane, can be catalytically dehydrogenated to the corresponding olefines according to the general reaction:

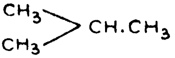
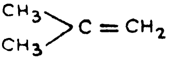
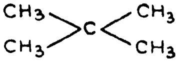
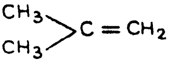
$$C_nH_{2n+2} \longrightarrow C_nH_{2n}+H_2$$

In this manner, and in almost every treatment of petroleum fractions, vast quantities of a whole range of olefines can be obtained. There are other processes such as alkylation, isomerisation, etc., but these have not such a pronounced bearing on synthetic rubbers and plastics.

To maintain the sense of proportion it should be added that hitherto the main urge has all the time been to produce more motor spirit. Indeed, during the last twenty years, the amount of petrol obtained from a given amount of crude oil has doubled. The olefines lend themselves very readily to conversion into such products, since they polymerise quite easily under heat and pressure to yield liquid hydrocarbons in the petrol range.

TABLE 19

CONVERSION OF PARAFFINS TO OLEFINES

REACTION			YIELD OF OLEFINE	
$CH_3.CH_3$ ETHANE	$\longrightarrow$	$CH_2 = CH_2$ ETHYLENE	$+ H_2$	100%
$CH_3.CH_3.CH_2$ PROPANE	$\longrightarrow$	$CH_3.CH = CH_2$ PROPYLENE	$+ H_2$	45%
	$\longrightarrow$	$CH_2 = CH_2$	$+ CH_4$ METHANE	55%
$CH_3.CH_2.CH_2\ CH_3$ n-BUTANE	$\longrightarrow$	$CH_3.CH_2.CH = CH_2$ 1-BUTENE	$+ H_2$	12%
	$\longrightarrow$	$CH_3CH = CH.CH_3$ 2-BUTENE	$+ H_2$	12%
	$\longrightarrow$	$CH_3.CH = CH_2$	$+ CH_4$	50%
	$\longrightarrow$	$CH_2 = CH_2$ HIGH TEMPERATURE	$+ CH_3.CH_3$	
	$\longrightarrow$	$2CH_2 = CH_2$	$+ H_2$	38%
 $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH.CH_3$ ISO-BUTANE	$\longrightarrow$	 $\begin{matrix}CH_3\\CH_3\end{matrix}\!>C = CH_2$ ISO-BUTYLENE	$+ H_2$	60%
	$\longrightarrow$	$CH_3.CH = CH_2$	$+ CH_4$	40%
 $\begin{matrix}CH_3\\CH_3\end{matrix}\!>C<\!\begin{matrix}CH_3\\CH_3\end{matrix}$ NEO-PENTANE	$\longrightarrow$	 $\begin{matrix}CH_3\\CH_3\end{matrix}\!>C = CH_2$	$+ CH_4$	100%

On the other hand, chemical manufacturers have concentrated on developing cracking conditions which give maximum production of simple olefines and a minimum production of motor spirit. While this applies to ethylene and propylene without qualification, the butylenes are not quite so amenable, and other uses have been sought for them. The influence of various catalysed treatments of isobutylene, for example, has led to the production of the polyisobutylene range of materials—ranging from very viscous liquids up to extremely rubbery products.

The Caterole Process. A new aromaticisation process has been developed in Great Britain by Weizmann & Bergmann.[38] Known as the Catarole Process, it makes possible the production of substantially pure aromatic hydrocarbons from naphtha or gas oil. It is a catalytic cracking process operating at 650–680° C. using metallic copper catalysts.

If petroleum is passed through a packed tube at atmospheric pressure at 630–680° C. and a velocity of 0·05–0·5 litres per hour per litre catalyst volume, the resultant liquid has an aromaticity of at least 95 per cent. In addition, valuable gaseous products are formed. The use of metals (such as copper) as packing materials reduces the temperature required for substantial aromatisation to 630–680° C. and also the extent to which carbon formation takes place. These two factors, combined with the purity of the products, make the process economical.

Below are listed the products obtained by aromatisation of a naphthenic heavy naphtha:

TABLE 20

AROMATISATION OF A NAPHTHENIC HEAVY NAPHTHA

Charge	
Spec. Grav.	0·798
Boiling Range (5–95%)	102–228° C.
Process Temperature	680° C.
Space Velocity	0·24
Liquid Product	
Recovery, by weight of charge	about 50%
Specific Gravity	0·870
Composition (on weight of charge)	
Boiling below benzene	1·8%
Benzene	11·8%
Toluene	10·7%
Xylenes, Ethylbenzene, Styrene	6·8%
Alkylbenzenes (150–180°C.)	3·4%
Above 180°C. (Polycyclics)	15·4%
Gaseous Product (composition by weight of charge)	
Hydrogen	0·3%
Methane	20·1%
Ethane	6·7%
Ethylene	7·8%
Propane	1·8%
Propylene	8·7%
Butanes	1·3%
Butenes and Butadiene	3·4%

The xylenes, etc., liquid fraction contains on an average 20 per cent styrene, 10·8 per cent ethyl-benzene, 16·2 per cent o-xylene, 19·3 per cent m-xylene, 24·7 per cent p-xylene.

The butenes, etc., liquid fraction consists of 60 per cent n-butylenes, 30 per cent isobutylene, 10 per cent butadiene.

Figures have been published for the production of olefines and aromatics from a tubular steam cracking unit processing 600,000 tons of heavy naphtha per annum. These figures are given in Table 20.

TABLE 21

OLEFINES AND AROMATICS FROM HEAVY NAPHTHA

Cracking Products	Tons
Ethylene, propylene, butylene, amylenes	260,000
Butylenes alone	35,000
Butadiene	14,000
Isoprene	4,000
Toluene	27,000
Benzene, xylenes	60,000

The Importance of Ethylene. For the moment let us refer back to ethylene. Its importance to the plastics industry cannot be overstressed. Something has already been described about its potentialities for the production of alcohol. This is being energetically pursued. It is estimated that the potential capacity of the oil industry in the United States is more than 1,000 million gallons of alcohols per year from cracked gases alone. This includes ethyl alcohol, propyl alcohols, butyl alcohols, etc., all of great importance to plastics, lacquers, and many other industries. These derivatives depend on having fairly pure ethylene which depends on the efficient separation of cracked gases. Latterly deep refrigeration methods have shown high promise in the efficient separation of the gases.

At the present time these olefines are being used for the manufacture of numerous glycols and related compounds.

Ethylene dichloride, in itself a very valuable and widely used solvent, is made by direct combination of ethylene and chlorine.

$$Cl_2 + CH_2{=}CH_2 \longrightarrow CH_2Cl{-}CH_2Cl.$$

Ethylene dichloride is used in large quantities in the manufacture of thioplasts, e.g. Thiokol, by interaction with sodium polysulphides. Thus another synthetic rubber-like material has a direct tie-up with the petroleum industry.

Recently, ethylene dichloride has acquired a greater significance from the plastics angle as a possible source for vinyl chloride. Brous,[7] has produced vinyl chloride by heating ethylene dichloride in the presence of methyl alcohol and adding aqueous sodium hydroxide.

Ethylene is also used to prepare ethyl chloride, one of the leading chemical intermediates at the present time. Together with benzene, when treated with aluminium chloride, ethyl benzene is obtained. This is the most important intermediate in the manufacture of styrene.

Ethylene reacts in chlorine water to form ethylene chlorhydrin. This may be readily converted into ethylene glycol. Ethylene glycol is of outstanding importance for the production of glyptal resins. Numerous other solvents, plasticisers and intermediates are also obtained from this reaction, including diethylene glycol, cellosolve, triethanolamine, etc.

The alkyl halides are of growing importance. Ethyl chloride may be synthesised via ethylene and hydrogen chloride.

Ethyl chloride and benzene, reacting under the influence of such catalysts as aluminium chloride, yield ethyl benzene, which is clearly the intermediate in the formation of styrene, and hence the styrene resins and rubbers.

Propylene is another constituent of petroleum wastes which is rapidly becoming more important. Propylene is readily converted into iso-propyl alcohol, a useful solvent, via propyl hydrogen sulphate, and the alcohol itself passes by catalytic dehydrogenation into acetone.

Williams[39] has developed the commercial synthesis of glycerol from propylene. Quite recently a commercial plant for the production of glycerol from propylene has begun to operate. The implications of this activity in relation to alkyd resins are obvious. It also marks a very notable step. From time immemorial glycerine has been obtained only from animal sources, from fats, etc., in soap-making. Allyl chloride is formed by the chlorination of propylene at high temperatures. Hydrolysis of this leads to allyl alcohol. After hydrochlorination the chlorohydrin is produced, which, with alkali treatment, yields glycerol:

Further derivatives prepared by well-known methods from propylene include: acetone, isopropyl ether, methyl-ethyl-ketone, ter-butyl alcohol, allyl alcohol, methallyl alcohol, acrolein and epichlorhydrin.

The dehydrogenation of isopropyl alcohol to acetone is now an accomplished fact and has greatly reduced the cost of acetone. Acetone may be condensed to diacetone alcohol, and this in turn dehydrated to mesityl oxide. It may then be further hydrogenated to methyl isobytyl ketone. Mesityl oxide is a solvent for polyvinyl chloride.

Acetone is easily converted to ketene by pyrolytic methods:

$$CH_3.CO.CH_3 \longrightarrow CH_2{=}CO+CH_4$$

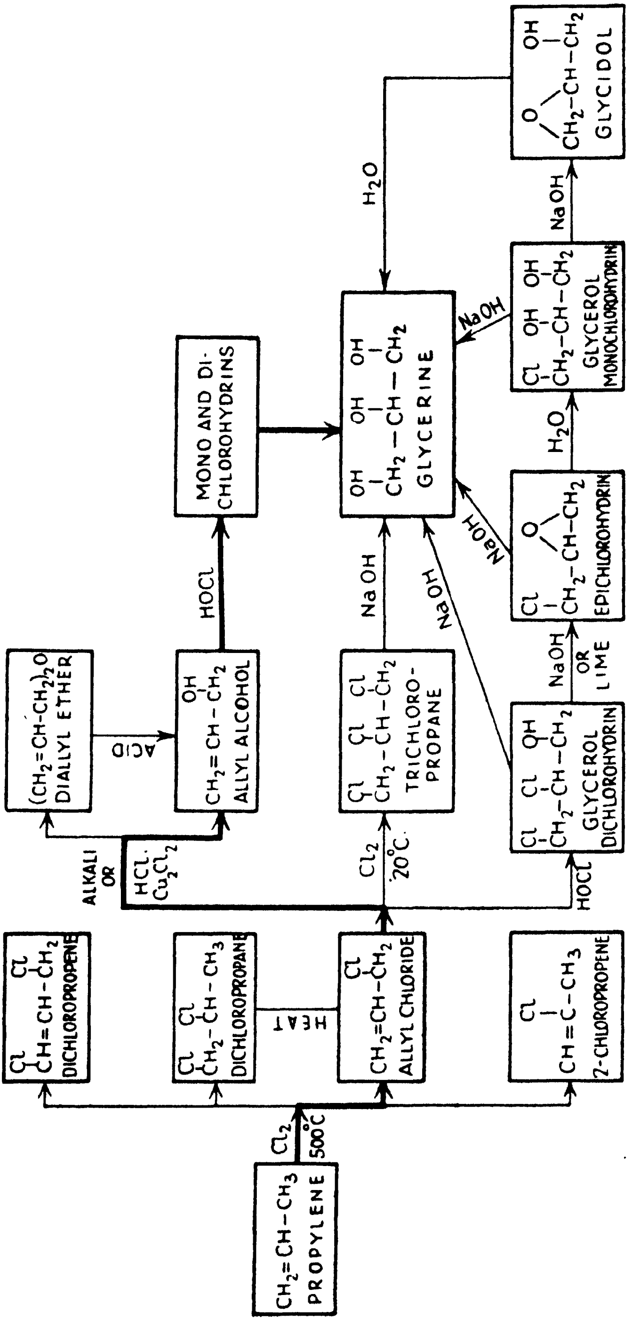


Fig. 20. Synthesis of glycerol from petroleum

Ketene with acetic acid yields acetic anhydride—an outstandingly important intermediate in the production of cellulose acetate and other esters. Furthermore, ketene readily polymerises to diketene and this yields in turn aceto-acetic esters.

The pyrolysis of methane to acetylene is of great importance. According to Dunstan about 10,000,000 tons a year of available hydrocarbon (mainly methane) is available throughout the world. Most of this is lost or burnt at the fields and refineries as fuel. From this vast quantity it is reasonable to assume that the production of not only acetylene but also aromatic hydrocarbons will be found profitable.

The production of phthalic anhydride from petroleum has already been mentioned. Standard Oil Company of California produces 4,000 tons per annum.[32] The process is the catalytic vapour-phase oxidation of o-xylene over a vanadium catalyst. The o-xylene is obtained as a petroleum by-product.

The products from acetylene have already been discussed. The point to be emphasised here is that high temperature cracking or pyrolysis of any petroleum fraction from methane to hydrocarbons of high molecular weight yields in effect a "synthetic" coal-tar. It follows that all the well-known derivatives of ordinary coal-tar—dyes, solvents, resins, plastics, explosives, detergents and the like are equally producible and obtainable from mineral oil—but in greater quantity and even more diverse in application.

Agriculture as a Source of Raw Materials for Plastics. It has recently become increasingly clear that agricultural products are likely to form a very important source of plastics in the future. Plastics has been an outstanding field for the successful application of agricultural products. This trend was strongly supported by Henry Ford. It has also been backed by the United States Bureau of Agriculture. It has recently received its greatest fillip from the synthetic rubber scheme. For plastics, the object is to convert agricultural products into chemicals which may be converted into plastic products, or directly into products which can be moulded under heat and pressure.

Cellulose as a base for plastics is, of course, well known. Cellulose derivatives have been very important for many years, and they continue to expand at a very great rate. More emphasis should be given to the surprising number of other plastics raw materials which are derived from agriculture and allied activities. There is a strong urge to convert agricultural materials into chemicals which may be employed as plastic bases, or which can be directly moulded under heat and pressure. Already there is a long list of such materials, e.g. furfural, lignin, soya bean, coffee, and so on. Apart from this, the production of ethyl alcohol, acetone and butyl alcohol are major industrial activities, having a very profound bearing on the plastics industry.

Alcohol as a source of ethylene is a leading material in the production of the newer thermoplastic types of synthetic resins. Another very important chemical is lactic acid which may be obtained from whey. Thus lactic acid and esters have been converted into acrylic derivatives by thermal decomposition. Since these plastics are in their infancy and seem destined for unpredictable expansion, their sources of raw materials are clearly important. This is merely a selection of some of the leading products, and is by no means exhaustive.

The outstanding advantages in the use of agricultural products is the fact that there is an annual crop produced based on oxygen, carbon dioxide and solar energy, catalysed by chlorophyll in the living plant. There is a yearly crop produced as cotton, linters, wood cellulose, straws, grains, cereals, etc. All are available in unlimited quantities. Moreover, quantities which do not diminish. This contrasts with other raw materials, notably such as petroleum, which, so far as is known, are in diminishing supply.

The possibilities of harnessing agriculture to industry have attracted great attention, notably in the United States and the U.S.S.R. The study of chemurgy, as the subject is known, has made considerable advances.

The Use of Agricultural Wastes. The use of agricultural products for plastics is one of the leading successes.

Apart from other factors it has been accepted that if agriculture can be harnessed to industry it would have a great stabilising influence. The war has given strong impetus to this trend. In many countries there have been surpluses of agricultural products which could not be disposed of, and great efforts have been made to utilise them. Apart from this, there are waste materials of every descriptions; waste wood and sawdust is a typical example. The crux of using waste materials is their availability. Wastes which build up as a consequence of other profitable activity can readily be used. Where collection and transport are difficult and introduce elements of cost, then the use of wastes may not be economic.

Three main principles provide the urge for developing industrial uses for agricultural products:

(*a*) The utilisation of waste materials and by-products.

(*b*) The introduction of new crops to take the place of imported crops at present used by industry.

(*c*) The development of new uses for crop surpluses.

TABLE 22

COMPOSITION OF SOME PLANT MATERIALS[14]

Plant Material	Cellulose %	Lignin %	Pentosans %
Bagasse	60·2	21·7	29·1
Cereal straws—			
Barley	48·6	16·4	31·9
Oats	43.8	18.5	22·8
Rice	45·5	10·9	21·5
Rye	36·3	11·3	20·4
Wheat	56·7	16·6	28·4
Cornstalks	38·4	34·3	27·6
Cotton	91·2	—	—
Flax	92·0	4·0	2·0
Hemp	79·3	5·2	5·5
Jute	74·9	11·7	18·1
Linseed straw	53·8	23·3	17·1
Ramie	85·0	1·0	2·0
Sisal	77·0	6·0	13·0
Wood-aspen (poplar)	62·1	26·5	17·6
Beech	67·1	22·5	24·9
Birch	64·2	19·6	27·1
Jack-pine	57·6	33·6	12·3
Pine	60·5	26·4	11·0
Spruce	60·9	30·2	12·6

There are vast quantities of agricultural wastes. The big snag is the high cost of collection and transportation for processing. This leaves no margin for the farmers. Most development with residues has been where they occur as by-products in standard forms of production in processing agricultural materials. For example, the use of bagasse, straws, and stalks, etc., in wall-board manufacture. The production of furfural from oat husks, by the Quaker Oats Company is another notable example.

The outstanding example of a new crop is the cultivation of soya beans in the United States, enthusiastically sponsored by Henry Ford. By 1937 there were 2,000,000 acres of soya beans, all designed for industrial purposes. In 1948 an acreage of 9·8 million acres produced a record 220 million bushels.

Another example is the cultivation of dandelions in the U.S.S.R. for rubber, which reached 650,000 acres in 1942.

At the present time the idea of surplus food crops appears incongruous; nevertheless, the Americans use grain and cereals as major raw materials for industry; the Russians use potatoes; so do the Germans. During recent world food shortages the use of agricultural materials has temporarily declined.

Groups of Agricultural Raw Materials. The raw products of agriculture are fundamentally carbohydrates, proteins, and fats. Agricultural raw materials can be considered in a number of groups which roughly correspond with these divisions.

Firstly, there are the various forms of cellulose obtained from cotton, from wood in the form of wood pulp, and from a variety of straws. The purer forms such as cotton afford unlimited quantities of the cellulose plastics, and also as filling materials generally. The cruder materials are also sources of lignin.

Secondly, there is the starch and sugar types of product, such as corn, wheat, potatoes, sugar cane, molasses, etc., which industrially serve as a primary source of alcohol or other chemicals by fermentation processes. These have acquired great significance because of the leading part they have played in the production of synthetic rubber in the United States, in the U.S.S.R., and in other countries.

The third group of materials include those which contain nitrogen, such as soya beans, beans, and lentils, etc., which contain protein. They behave in many respects like casein from milk. Casein, obtained from milk, has been the basis of one of the oldest activities in the plastic industry. It appears to be taking on a new lease of life for the production of synthetic fibres.

Fourthly, there are the obvious agricultural wastes such as stalks, husks, hulls, straws, etc., which are primary sources of furfural; a fifth group comprises wood waste, such as sawdust, cut off pieces, etc., which are sources of alcohol, lignin, and so on.

Cellulose Derivatives. Cellulose plastics are a major group.

The leading products are cellulose acetate, cellulose nitrate, ethyl cellulose, and various other esters and ethers. Many thousands of tons of pure cellulose are used in their production every year, and a further large quantity is employed as filling material. In 1941 30,000,000 pounds weight of cellulose acetate were used for moulding purposes in the United States alone. In 1946 together with cellulose acetobutyrate and ethyl cellulose the figure had risen above 90 million pounds.

Cellulose is found in walls and cells of all vegetable matter. Cotton is a very pure form, while cotton linters consist of more than 90 per cent cellulose. The most desirable cellulose raw material is consequently cotton linters, i.e. the short fibres remaining on the seed after the long fibres have been removed for spinning. Approximately 175 pounds of cotton linters are obtained per ton of cotton seeds. There is large-scale production of cotton in many countries.

It must be remembered that the use of cellulose in plastics is very small compared with uses for rayon.

TABLE 23

CELLULOSE PLASTIC PRODUCTS

Cellulose Nitrate

Year	Sheets lb.	Rod and Tube lb.	Total lb.
1938	6,617,000	2,871,000	9,488,000
1941	10,893,000	5,606,000	16,499,000
1946	10,932,000	7,229,000	18,161,000
1947	9,000,000	3,600,000	12,600,000

Cellulose Acetate

Year	Sheets, Rods and Tubes lb.	Moulding Powders, etc. lb.	Total lb.
1938	6,831,000	7,394,000	14,225,000
1941	6,218,000	30,717,000	36,935,000
1946	19,864,000	83,204,000	103,068,000
1947	19,000,000	60,000,000	79,000,000

Ethyl Cellulose, etc.

Year			Total lb.
1946			12,183,000
1947			4,000,000

Thus, United States production of rayon alone in 1948 was 1,120 million pounds.

Wood pulp has been purified in the United States and Sweden to serve as raw material for cellulose. The products are not quite as good as those derived from linters, but are definitely satisfactory. Wood pulp is the main material used for preparation of the various viscose products. It is not yet widely used for plastics, although the trend is growing. Apparently the cellulose in wood pulp withstands the chemical treatment involved in making plastics. It has to be purified in order to remove deleterious materials. Olsen[27] has outlined the relative chemical composition of some of these materials.

The absence of cotton or wood in any country is not an insuperable bar to the production of cellulose derivatives. This has been demonstrated in practice by the Pomilio process based on straws which are available in most countries.

TABLE 24

Cellulose	α-Cellulose	Soln. in Boiling 7% NaOH %	Pentosan %	Ash %	Permanganate No.	Viscosity in 2·5% Concn. Centipoises
1. Cotton Linters .	98·5	<2·5	<2	0·1	0·25	500–10,000
2. Bleached sulfite pulp	85·88	15–20	7–15	0·5	0·5	50–100
3. High α-cellulose pulps	93–96	5–8	3–5	0·1	0·5	50–300
4. Acetylatable wood pulp from Cellulose Research Corp . .	>98·5	<2·5	<2	<0·1	0·25	500–25,000

Pomilio Process for Obtaining Cellulose from Straws,[28] etc. Straws of every description, grasses, and agricultural by-products are used for the production of high-grade cellulose in Italy, Argentine, Chile, South Africa, etc. The leading method is the chlorination process developed by Pomilio. In brief the process is to—

(*a*) Digest the straws for a short time (about 2 hours at moderate temperature with weak alkali solution).

(*b*) Expose the digested, spongy mass to moist chlorine gas in the cold for 1½ hours.

(*c*) Treat the washed chlorinated mass with weak alkali and washing, taking about ½ hour.

(*d*) Gentle bleaching with dilute hypochlorite solution.

More than 95 per cent of available cellulose is obtained. Time required totals only 4 hours, which is very rapid for cellulose products. The process is continuous.

By this method, Italy, one of the largest rayon-producing countries, had become virtually independent of outside sources of supply.

The Alcohol Processes. The most spectacular application of all agricultural derivatives has been perhaps the use of alcohol for making synthetic rubber. At one time nearly a quarter of a million tons of synthetic rubber per year was being made in the United States on the basis of alcohol obtained from grain. Alcohol and other similar derivatives were being produced by extremely rapid fermentation processes from almost every farm product containing carbohydrates or sugar, e.g. from wheat, from corn, from sugar-beet, from potatoes, and so on.

TABLE 25

PRODUCTION OF ALCOHOL[20]

Raw Material	Alcohol Yield	
	Gal./acre	Gal./ton
Sugar-beet	287·0	22·1
Sugar-cane	268·0	15·2
Jerusalem artichokes	180·0	20 0
Potatoes, white	178·0	22·9
Potatoes, sweet	141·0	34·2
Apples	140·0	14·4
Raisins	102·0	81·4
Grapes	90·4	15·1
Corn	88·8	84·0
Rice (rough)	65·6	79·5
Molasses (blackstrap)	45·0	70·4
Grain sorghum	35·5	79·5
Wheat	33·0	85·0

American production of alcohol for 1944 was more than 631,000,000 gallons. Produced from molasses, grain, petroleum, natural gas, sulphite liquors, and wood waste.

Alcohol, apart from its application for synthetic rubber, is one of the most versatile of chemicals, having a wide application particularly in the production of the newer types of synthetic resins. Much of its behaviour has already been discussed in relation to ethylene. Many transparent plastics, such as methyl methacrylate polymer, polystyrene, and so on, are ultimately based on alcohol as raw material. Alcohol is also being obtained from waste wood.

The U.S.S.R. has for many years produced synthetic rubber based on alcohol, obtained mainly from potatoes. Other countries such as Britain and the U.S.A. have obtained alcohol mainly from molasses, derived from sugar-cane in the West Indies. As alcohol acquires increasing industrial importance other sources are being developed.

In normal times the United States has large surpluses of grain and other agricultural products. Produced in vast quantities every year, generally in excess, there is much waste. All these are suitable sources of alcohol. Alcohol acquired outstanding interest as a leading raw material for making butadiene for synthetic rubbers. But it is equally suitable as a raw material for synthetic resins.

The preparation of alcohol from these materials is based on established fermentation processes. These are operated on a very large scale, and present few difficulties. The general procedure is to place suitably ground corn, wheat, etc., into enormous vats. They are allowed to ferment, assisted by the use of enzymes, and form a mash. The material is then distilled for alcohol.

The residue is valuable cattle feed of high food value.

Improved accelerated methods of fermentation have latterly been developed which improve the production of alcohol. Thus, the latest methods in the United States show a yield of 2·5 gallons per bushel of corn, and 2·7 gallons per bushel of wheat.

It is interesting to note the relative status of various crops as regards the amount of alcohol that can be produced. The Russians have greatly increased the efficiency of alcohol production from potatoes. They claim to obtain 600 gallons per acre. It is a fact that in using potatoes as a source of alcohol, all may be used whether they are large or small.

In the United States during the earlier stages of synthetic rubber production, alcohol played a leading part in the manufacture of butadiene. However, from an economic point of view the trend eventually went against alcohol and in favour of petroleum processes. World food shortage has finally pushed alcohol out of the picture.

The major portion of butadiene obtained from alcohol was made by the Carbon and Carbide Union,[9] based on alcohol, chiefly derived from corn and wheat. They developed a very successful process, and led the way in getting into production. It is of interest to consider this more closely since butadiene is acquiring importance as a secondary monomer in the production of commercially important plastic copolymers. For example, it is used with styrene for materials such as Styralloy, etc.

The Carbon and Carbide Process. Alcohol and acetaldehyde are catalytically converted into butadiene. This is separated from the by-products and unchanged alcohol and acetaldehyde, which are re-used. The converters consist of 753 steel tubes, 20 ft. long by 3 in. diameter, containing catalyst. The tubes are surrounded by a temperature regulating bath of "Dowtherm" liquid. A 20,000-ton unit possesses

12 such converters, 4 converting alcohol to acetaldehyde by means of one catalyst, and 8 making the butadiene with another catalyst. So that it is a two-stage process. The yield is about 2·3 pounds of butadiene per gallon of 95 per cent alcohol. The catalyst becomes foul after a time, and it is cleaned by passing air over to burn off the carbon. During a single passage, about 10 pounds of the alcohol mixture has to be vaporised to give 1 pound of butadiene, the remainder being re-cycled, and used again. The butadiene is obtained 97 per cent pure.

TABLE 26

CHEMURGIC CHEMICALS IN USE EACH YEAR

	Tons
Waste cellulose material	200,000,000
Potential production of:	
Ethyl alcohol (U.S. process)	14,000,000
(Scholler)	60,000,000
Furfural	30,000,000
Cellulose	80,000,000
Lignin	60,000,000
Vanillin	15,000,000
Ethyl alcohol production from:	
Ethylene gas	230,000
Grain (whisky)	860,000
Blackstrap residues (domestic)	230,000
Molasses	570,000
Ethyl alcohol usages:	
Explosives	180,000
Anti-freeze	360,000
Solvents, lacquers, and plastics	720,000
Fuel	180,000
Synthetic rubber	1,800,000

Considering both this process from the engineering point of view on a large scale, it is clear that the vaporising of alcohol is not a difficult operation, nor is the passage over a catalyst. This contrasts with the complex high-pressure arrangements involved in the case of the petroleum derivatives, and also the somewhat involved chemical synthesis working from carbide. Of course, the butadiene in all the processes must be collected, separated, and purified.

Other Fermentation Products. During the last war Weizmann[37] developed the fermentation process which is second only to alcohol fermentation in importance. This was the process which produces butyl alcohol and acetone as chief products. The bacteria called *clostridium aceto-butylicum* acting on molasses, starches, grains, etc., produces the solvents in the ratio of—

Butyl alcohol	60 parts
Acetone	30 parts
Alcohol	10 parts

About 1½ times as much gas is formed, 60 per cent being carbon dioxide. Much of the remainder is hydrogen. The gases are caused to combine under pressure to yield methyl alcohol. The remaining carbon dioxide is made into solid carbon dioxide. All the materials produced are of the greatest importance to plastics activities. Butyl alcohol, or butanol, is important as a solvent. But its great significance to the plastics field is as parent material for plasticisers. From it is made dibutyl phthalate, almost the most outstanding plasticiser.

The Butylene Glycol Process. There is another process which should be mentioned in connection with agricultural products. This is the method developed at the Iowa University. The chief personalities connected with it are Christensen and May.[10] They start with any material containing starch or sugar. This is fermented in the presence of an enzyme known as *aerobacter aerogenes.* The material is fermented for about 40 hours, and a yield of 84 per cent of the theoretical quantity of 2·3-butylene glycol is obtained. There is no production of alcohol. The separation of butylene glycol has been a matter of some difficulty, but has been achieved by the use of acetic acid. By using this, 2·3-butylene glycol diacetate is formed which can be separated. This is passed through heated tubes without any catalyst and yields butadiene. One snag in the past has been the use of large quantities of acetic acid, involving high losses, but now a 99 per cent recovery can be obtained. The production is between 6·8 to 7·8 pounds of butadiene per bushel of corn. The butadiene obtained in this way is practically pure and can be used directly. There are many other promising fields of application for this butylene glycol in the plastics industry, e.g. for alkyd resins.

Wood for Alcohol and Other Chemicals. Off-cuts and sawdust abound in most countries. They are often a source of embarrassment and are usually burned. Wood waste of every description is an enormous potential source of plastics. Important materials are alcohol, other fermentation products, and lignin. There is much activity in this field in the United States, in the U.S.S.R., and in Canada. It has been calculated that the whole annual wood waste of the United States is equivalent to approximately 4,000 million gallons of alcohol, at a yield of 50 gallons per ton of wood.

Production of alcohol from wood is carried out along two main systems:

American Wood Process.[3] The principle on which this is based is that wood is a plentiful material.

Soft wood waste as sawdust or shredded wood is digested with an equal amount of dilute sulphuric acid under direct steam at 125 lb. per sq. inch pressure for 15 minutes. Up to 25 per cent weight of the wood is converted to sugar of which 75 per cent is fermentable. Residual lignin contains material which is suitable for moulding purposes.

Scholler Process.[29] This German method is based on the fact that wood is a scarce material. They completely convert wood cellulose to sugar. The method is to digest sawdust or shredded wood with dilute sulphuric acid, under 175 lb. steam pressure at 190° C. for about 16 hours. A 6 per cent sugar solution is obtained which is fermented to alcohol.

Alcohol Production using all Sawmill Waste. The usual estimate of waste from mill operation is approximately 1 ton for each 1,000 feet of lumber cut.

The cheapest wood waste is sawdust, comprising about one-third of the total mill waste. It is already in the physical form suitable for hydrolysis without further processing. Therefore it has been found that the minimum mill that could operate on sawdust alone must be three times the size of one turning all its waste into chemicals. In order to support a hydrolysis plant using the American process, this mill must cut about 150,000,000 feet a year.

Seventy tons of wood per day, or a daily cut of 70,000 feet of lumber would be required to support a Scholler plant capable of producing 3,600 gallons of alcohol per day, at a yield of 50 gallons of alcohol per ton of wood. Such a mill would cut 20,000,000 feet annually. An alcohol plant of the same capacity using the American process at a yield of 20 gallons per ton of wood would require 180 tons of wood per day, the waste from a daily cut of 180,000, or roughly, an annual cut of 54,000,000 feet.

Sulphite Liquor Process. Vast quantities of sulphite liquors are run to waste from paper manufacturing establishments in every country. Yet production of alcohol from sulphite waste liquor is technically simple. Sugars are produced as a by-product of the pulping operation, which is a mild acid hydrolysis. Three-quarters of the sugar produced is fermentable by ordinary yeasts. The sugar content of the waste liquor varies according to the kind of wood, the cooking schedules, and acid concentrations used in the process. According to Hall[18] the production of a ton of pulp is accompanied by approximately 1,200 gallons of waste liquor with a fermentable sugar content of 2 per cent. There are approximately 190 lb. of fermentable sugar per ton of pulp. About 12 gallons per ton of pulp produced is a normal yield, i.e. about 75 per cent.

In processing, the waste pulp liquor is aerated to remove free sulphur dioxide, cooled, limed to raise the pH to about 6, separated from sludge, fermented for about 48 hours, and distilled.

Steam consumption is important in the production of alcohol from sulphite waste liquor. It is high because the alcohol solutions obtained are very dilute. About 80 pounds of steam are required for the distillation of 1 gallon of alcohol (95 per cent) from a feed liquor of 1 per cent alcohol, compared with only 18 pounds per gallon for a feed liquor of about 8 per cent alcohol as obtained from molasses.

Furfural. It is obvious there is an enormous amount of waste material available from agricultural sources every year in the form of corn stalks, corn cobs, oat hulls, a whole variety of straws and stalks, and so on. Every country has them; very little is done with them. In the United States, for example, it is stated that 400 million tons are available every year. In general they are an embarrassment, and are burned. However, efforts have been made to utilise part of them. They have a number of interesting possibilities. Some have been suggested as possible sources of cellulose. There are, however, two materials present in most of them which have attracted interest—one is furfural, and the other is lignin.

Furfural is produced on a commercial scale chiefly from oat hulls. Present output is of the order of 50 million pounds per annum. It is a light brown liquid, colourless when pure, boiling at 164°C. It resinifies very easily. The production has depended upon the fact that very large supplies of oat hulls are produced at a convenient location as a by-product of other commercial manufacture. The Quaker Oats Company has been a pioneer in this field. By one method the pentozans present are hydrolysed by means of a mineral acid, and the furfural formed is separated by steam distillation. One procedure is to place 3 tons of ground hulls in an acid-resisting steel rotating digester. Some 1,500 lb. of water and 100 lb. of concentrated sulphuric acid are added. The furfural is finally separated by passing live steam through, and the material is subsequently fractionated to the desired degree of purity. By a method of this type Miner and Brownlee[23] obtained a yield of 10 per cent on the weight of the hulls.

Another simple method is to treat these wastes by destructive distillation to give pyroligneous acid, neutralising the acid with lime, thereafter distilling furfural.

Lignin as a Raw Material for Plastics. Lignin is one of the most widely available materials owing to the fact that it is a major ingredient in wood. It has definite possibilities as a basic material for plastics. Many investigators have aimed at using waste wood and sawdust for moulding compositions. Numerous articles have already been produced from it. Much work has been carried out to develop commercial uses for lignin which is available in enormous quantities, particularly in the United States and in the U.S.S.R. Work has been carried out along two paths.

In the one case lignin has actually been separated. This activity is chiefly carried out with waste liquors from the sulphite process for making paper. The other method, based on wood, etc., has been to try to prepare a plastic *in situ*, using the wood cells present as filling material.

In the United States the Forest Products Laboratory has prepared many useful chemicals from lignin by hydrogenation in the presence of catalysts, such as chromium oxide.

The processing of a ton of lignin has already given the following materials:

15	gallons methyl alcohol
300	pounds mixed phenols
800	pounds neutral oil
300	pounds heavy oil

According to Sherrard and Harris[31] one fraction could be made to form a hard fibrous resin.

Most work has been done to make lignin-cellulose materials, since both exist together in wood. In this instance it is essential to break up the continuous cellulose structure and a number of methods have been developed to do this.

One group of ligno-cellulose products is obtained by charging chips into a cylindrical steel vessel equipped with a loading port at the top, a quick opening hydraulically operated discharge valve at the bottom, and a steam inlet. The "gun," as the vessel is called, is filled with chips and closed, saturated steam is allowed to enter until a pressure of 600 lb. per sq. inch is reached. It is then quickly increased to 1,000 lb., held at that pressure for approximately one or two seconds, and then quickly discharged from the gun into a cyclone. The chips explode owing to the high internal pressure. The fibre falls into a storage tank, is mixed with water in a ratio of 3 parts of fibre to 97 parts of water, and is then pumped through refiners, screened, and conveyed to a stock chest. It is then formed into boards, a waterproofing compound being added to the stock. These boards, cut into 12 ft.

lengths, are conveyed, twenty at a time, to hydraulic presses. The length of time the boards remain in the press is determined by the density of the product desired.

"Benalite,"[4] a lignin-plastic material, is produced from either hard or soft woods. The wood is subjected to the same pre-heating treatment, but is held in the reactor at high steam pressure for a considerably longer period under controlled pH conditions. It is formed into sheets, and the moisture content is reduced to 5 per cent. The sheets are put into a flat-bed press and subjected to a pressure of from 1,500 to 2,000 lb. per sq. inch at sufficient temperature to cause conversion to the cured state. "Benalite" has a specific gravity of 1·44. It may be turned, tapped, and sawn, and it is also adaptable for the production of moulded containers.

Bogdanov[6] in the U.S.S.R. has developed a process employing lower temperatures. Pinewood sawdust is heated with 1 to 5 times its weight of water for 2 hours at 170° C. and 115 lb. pressure. A powder is formed which can be dried and moulded. The addition of phenol increases the flowing characteristics of the material. A pressure of 5 tons per sq. inch was used for moulding up to a temperature of 250° C.

According to Grant,[15] wood hydrolysed by dilute sulphuric acid at 120 lb. per sq. inch for three-quarters of an hour, can also give a plastic moulding material.

Lignin reacts readily with aldehydes, notably with furfural, and advantage has been taken of this to make some interesting materials.

Another method developed in the U.S.S.R. by Losev, Kaminskii, and Schiskin,[22] treated 47 per cent lignin with 8 per cent furfural and aniline in the presence of 3 per cent lime to give a useful moulding powder.

Sheets of lignin plastic can be surfaced with synthetic resins in various colours or can be left with a lustrous black finish. It is made in a range of thicknesses as flat panels. Its electrical properties are favourable for ordinary insulation purposes. It may be drilled, tapped, or turned readily. The possible commercial applications of this type of plastic have just begun to be explored. The low cost of ingredients have made this plastic of interest for industrial applications involving large quantities of material, such as building units, furniture, and wall panelling, etc.

Soya Beans. The soya bean is an amazing product of which a great deal has been heard. It is the outstanding example of a crop deliberately cultivated for industry, and it has an enormous technical value. The soya bean is a source of raw material for the plastic industry. From a ton of soybeans are produced about 250 pounds of oil and

1,600 pounds of meal, containing approximately 40 per cent protein. This raw material is proving to be an excellent source of material for the plastic industry. America produced about 40,000,000 bushels of soybeans. If 40 per cent of this is protein, it is evident that the soya bean is an extensive source of plastic material.

No part is wasted. After the oil has been extracted, the soya bean meal is converted into a moulding powder together with phenol and formaldehyde. It gives moulded articles of improved strength, and at low cost. The Americans obtain 25 bushels of soya beans per acre, yielding about 600 lb. soya bean protein, suitable for plastics.

TABLE 27

COMPOSITION OF SOYA-BEAN MEAL AFTER OIL EXTRACTION

	Percentage Composition
Dry substance	91·85
Crude protein	41·41
Ether extract	5·05
Ash	5·70
Crude fibre	7·50
Total nitrogen	6·63
Calcium	0·273
Phosphorus	0·454

The Ford Company is probably the greatest user of these plastics, and it proposes to use them on a large scale in its plastic cars of the future. Protein both from casein and soya bean have been converted into very attractive fibres, which in many respects resemble wool. It is also interesting to notice that soya beans are the basis of a form of synthetic rubber developed in the United States, called Norepol.[26]

Use of Cashew Nut Shell Liquid in Resins. An interesting and commercially important series of resins is obtained from cashew-nut shells. These are mainly derived from India. Morgan[24] has described these in some detail.

The cashew nut has a shell about one-eighth of an inch thick, inside which is a soft honeycomb structure containing a viscous liquid which completely enclosed the kernel. This viscous liquid provides the raw materials from which cashew resins are made; it is poisonous and has a strong vesicant and dermatitic action on the human skin. The industrial importance of the liquid has been realised only in America, where it was imported in large quantities. The constitution of the liquid and the industrial development of cashew resins and polymers is due mainly to the work of Harvey. The liquid contains two phenols —cardol and anacardic acid. The former is a resorcinol derivative with a long-chain substituent group containing two double bonds, the position of which has not yet been determined. Anacardic acid is a salicylic acid derivative containing the same substituent groups as has been found in cardol; it decarboxylates smoothly on thermal treatment to give a monohydric phenol known as anacardol. The first step in processing the crude imported material is an acid treatment; this removes metallic impurities and traces of sulphur compounds present in the oil. The treated oil can then be used as the resin-making raw material or can be separated into two portions by steam distillation. The steam distillate, amounting to about 70 per cent of the total, contains a monohydric phenol known as cardanol. The non-steam-distillable portion contains cardol and polymer formed during the processes of extraction and treatment.

Acid polymerisation of cashew nutshell liquid can be made to give an intermediate polymer which is a brown viscous liquid capable of reacting in the cold with aldehydes such as paraformaldehyde or furfuraldehyde. Cold-setting cashew nutshell liquid compositions of this type possess excellent acid and alkali resistance and find extensive use as stopping and filling compounds in the electrical industry, in industrial floorings and chemical plant of the "Haveg" type, where good alkali resistance is a prime requisite. Fully thermo-hardened resins ground to coarse dusts are used as friction-modifying materials in the manufacture of brake linings, clutch facings, and other frictional elements. The acid polymers when reacted hot with hexamine give soft rubbery polymers of good compatability with natural and synthetic rubber. The ultimate acid polymer of cashew nutshell liquid is also rubber-like, and has a very low susceptibility to oxidation. The distillation residue of high cardol content can also be acid-polymerised, and these polymers can be reacted further with aldehydes. The products are characterised by outstanding heat resistance.[19]

Like phenol, both cashew nutshell liquid and cardanol can be reacted directly with aldehydes to give resins. These resins, however, have several characteristics not found in phenol or cresol formaldehyde resins. Most important of these are the relative flexibility of the resin in the fully cured state, its solubility in both aliphatic and aromatic solvents, and the high degree of resistance to caustic alkalis.

REFERENCES

1 Alcohol Production. *Ind. Eng. Chem.*, 1944, **36**, 12.
2 AMBROS. Kunstoffe, 1939, **29**, 106.
3 American Wood Process. U.S. Senate Sub-Committee on Agriculture and Forestry, 1943, p. 1499.

4 Benalite. Mason, Boehm, and Koome, U.S.P. 2,080,078/1937.
5 BINGHAM. *J. Soc. Chem. Ind.*, 1918, **85**, 37.
6 BOGDANOV. *Plastics*, 1942, **6**, 247.
7 BROUS. U.S.P. 2,041,814/1936.
8 BURTON. U.S.P. 1,049,667/1912.
9 Carbide and Carbon Process. U.S. Senate Sub-Committee on Agriculture and Forestry, 1943, p. 1257.
10 CHRISTENSEN AND MAY. *India Rubber World*, 1942, **104**, 477.
11 DUNSTAN. *Chemistry and the Petroleum Industry*, 1942.
12 FREY AND HEPP. "*Science of Petroleum*," Oxford Univ. Press, 1939, p. 1944.
13 FRÖLICH. *Ind. Eng. Chem.*, 1940, **32**, 293.
14 GRANT. *Plastics*, 1942, **6**, 247.
15 GRANT. "*Laboratory Handbook on Pulp and Paper*," Arnold & Co., London, 1942.
16 GROSSE AND IPATIEFF. *Ind. Chem. Eng.*, 1940, **32**, 268.
17 GROSSE, MORELL AND MAVITY. *Ind. Chem. Eng.*, 1940, **32**, 309.
18 HALL. U.S. Senate Sub-Committee on Agriculture and Forestry, 1943, p. 1498.
19 Harvel Corp. B.P. 599, 198/1948.
20 JACOBS. *Ind. Chem. Eng.*, 1939, **31**, 165.
21 JONES. *Chemistry and Industry*, 1943, **62**, 66.
22 LOSEV, KAMINSKII AND SCHISKIN. *J. Org. Chem. Soc.* (U.S.S.R.), 1937, **4**, 620.
23 Miner Process. *Ind. Chem. Eng.*, 1936, **19**, 1217.
24 MORGAN. *Chemistry and Industry*, 1945, **64**, 70.
25 MORRISON. *Chemistry and Industry*, 1941, **60**, 388.
26 Norepol. *Rubber Age*, 1943, **24**, 65.
27 OLSEN. *Ind. Eng. Chem.*, 1938, **30**, 525.
28 POMILIO. *Ind. Eng. Chem.*, 1939, **31**, 657.
29 Scholler Process. U.S. Senate Sub-Committee on Agriculture and Forestry, Washington, 1943, p. 1500.
30 SCOTT. *Chemistry and Industry*, 1944, **63**, 274.
31 SHERRARD AND HARRIS. *Ind. Eng. Chem.*, 1932, **24**, 103.
32 Standard Oil of California. *Chem. Eng.*, August, 1946.
33 TUGENDHAT. *Trans. I.P.I.*, 1943, **11**, 31.
34 United States Production of Plasticisers. U.S. Bureau of Tariffs.
35 WAKEMAN AND WEIL. *Ind. Eng. Chem.*, 1942, **34**, 1387.
36 WEISS. *Chem. and Eng. News*, Jan. 26, 1948.
37 WEIZMANN. B.P. 4845/1915.
38 WEIZMANN AND BERGMANN. B.P. 552, 216; 552, 115; 575, 383.
39 WILLIAMS. *Chem. Met. Eng.*, 1940, **47**, 834.
40 B.I.O.S. Reports No. 137 and 266, item 22.

CHAPTER III

PLASTICS ARE BASED ON LARGE MOLECULES

SINCE there are so many different plastics, it is desirable to note the outstanding feature which they all have in common. They are all materials which have very large molecules. In most cases the molecule is so large that the molecular weight cannot easily be determined. Staudinger[13] has coined the term "*macromolecule*" to apply to these large units, to imply that they are of a different order of magnitude to ordinary molecules.

Most of the desirable characteristics of plastic materials are due to these large macromolecules. Carothers[3] attributes all the outstanding physical and tensile characteristics of the materials to this fact.

"The most important peculiarity of high polymers is that they alone among organic materials to a significant degree show such properties as strength, elasticity, toughness, pliability, and hardness.

Weight for weight, cellulose and silk are stronger than steel; rubber exhibits a combined strength and elasticity that is not approached in anything in the organic world, while diamond is harder than any other material.

The practical uses of high polymers depend almost entirely on these mechanical properties. Our clothing and furniture, and much of our shelter is made of such materials. The names cellulose, wool, rubber, and silk suggest at once the great importance of the non-chemical uses of high polymers."

Plastics are all formed by building up these large macromolecules, starting from small ordinary molecules. In other words, the chemist starts with simple chemicals, such as phenol, formaldehyde, alcohol, acetylene, and so on.

By modifying them, rearranging them, and then joining molecule to molecule, he builds up giant macromolecules never found in nature. This is the process underlying most of the plastics from phenol-formaldehyde resins to nylon.

Polymerisation. The process of building up large groups based on recurring units is known as *polymerisation*. Understanding of the mechanism of polymerisation is the key to a thorough grasp of the subject of plastics. It is necessary to resort very freely to analogies in order to explain current ideas on the subject.

The two main groups of plastics are based on thermosetting resins, and on thermoplastics. The behaviour of thermosetting resins in their formation and subsequent treatment is different from the behaviour of the thermoplastic polymers. There are some features in common.

Thermoplastics in turn divide up into several main groups, namely, (*a*) thermoplastic polymers, i.e. the vinyl family of materials such as polystyrene, polyvinyl chloride, polythene, etc., and (*b*) thermoplastic cellulose derivatives.

Thermoplastic polymers are made by the joining up of a number of simple *monomers*. A monomer is a simple chemical entity which can be built up by polymerisation.

The Polymerisation Process. A monomer is a chemical entity such as styrene, vinyl chloride, vinyl acetate, methyl methacrylate, and so on, in the vinyl series, or such as butadiene, isoprene, chloroprene, etc., in the diolefine (or divinyl) series. It will be noted that each monomer is unsaturated. It has at least one double bond. This is a necessary condition for it to be able to polymerise.

Polymerisation is generally regarded as the linking-up of a number of these monomeric units into long open chains or macromolecules. This is the Staudinger conception, which is widely accepted. Each monomer unit forms a link in a straight uninterrupted chain. The unsaturation of each unit has disappeared in the polymer in those cases where only one double bond existed. One double bond in each unit is always lost in polymerisation.

According to the treatment and the conditions, it is thought that chains of various lengths are formed. The properties of the product depend upon the extent to which polymerisation is carried out, or, in other words, to the length of the chain. The molecular weight of the product (generally determined by the viscosity) gives the measure of the degree of polymerisation. As the length of the polymer increases so the valuable mechanical properties become more apparent.

The character of the material changes, generally from the liquid state, since most monomers are liquids. These become more viscous, and then perceptibly change over towards the solid state. The various monomeric butadiene derivatives change to rubbery solids, and so on. Liquid styrene ultimately changes to the solid, glassy polystyrene, having remarkable electrical properties. Gaseous vinyl chloride, which actually boils at $-14°$C., forms the tough, strong polyvinyl chloride. Liquid ethyl acrylate becomes a somewhat soft, glassy, solid, flexible polymer, but having exceptional mechanical strength. Methyl methacrylate polymerises to much harder transparent solids, which have remarkable light transmission. The straight chains initially formed by polymerisation may tend to become cyclised by linking along the chain.

The commercial value of these highly polymerised materials arises out of their unique properties, notably those of a mechanical nature, namely, great strength, elasticity, toughness, and pliability. They are also generally transparent and resistant to corrosion. Another important aspect from the commercial angle is the fact that there is no waste incurred in the polymerisation process. *There are no by-products.*

In the case of materials, such as the cellulose plastics, casein plastics, etc., the long molecular structure is already there having been built up by nature. Most plastics activity with these materials involves modification of appendages to the long chain, and even to the breaking down or shortening of the chain to some extent.

Structure of Polymers. During the last thirty years, a vast amount of work has been carried out in polymerisation, notably by Staudinger, Carothers, Mark,[6] Whitby,[16] Marvel,[10] Melville,[11] and their colleagues.

All the work carried out by these authorities almost unanimously leads to the conclusion that high polymers generally, whether natural or synthetic, are made up of enormous molecules containing hundreds or thousands of atoms bound together. A word of caution is necessary about these "enormous molecules." The largest synthetic long molecule made does not exceed 100,000 Å., which is still less than one-hundredth of a millimetre in length! There seems general agreement that many naturally high polymers such as rubber, cellulose, silk, etc., have a long molecule in the form of a long chain or thread. It seems likely also that in these materials the number of cross linkings between adjacent long molecules is very small. In other words, each long chain is an individual unconnected macromolecule. This particularly seems to apply to cellulose and its derivatives.

The building-up process, or polymerisation process, can take a number of forms. There can be growth entirely in one dimension, in length, in which case thread-like polymers are obtained. This is the case with most simple thermoplastic materials. In these instances the growth of the molecule can fairly easily be followed. Consider thousands of these molecules in free fluid motion. At ordinary temperature there is no tendency or little tendency for any ends to join together. Then energy is imparted to the system possibly with the aid of some catalyst. Immediately, the ends begin to join up. It has been suggested that these might take place by some single units becoming highly energised.

When such an active unit has joined up the energy is passed on to another unit which also proceeds to join, and so on.

Whatever the mechanism the units build up. The monomer units are still considered to retain much of their freedom of movement in the chain, and are assumed to be vibrating according to their nature. Then, according to molecular weight determinations, instead of an assembly of short units, they could build up possibly to a thousand units, i.e. the macromolecule will be a thousand times as long as a unit. Clearly the freedom of action of such a long unit would be very limited as compared with the original molecular entities. So the whole system tends to build up into units which may approximate to this thousand type. Owing to the loss of freedom of movement the fluid system has changed into a substantially solid system without flow which comprises all these long chains intermeshed in all directions. This is substantially the situation existing in simple thermoplastic synthetic resins.

The subsequent behaviour is bound up with the movement of these very long molecules in relation to each other. The long units will be vibrating and moving about by virtue of their own intrinsic energy, but they will be too tangled together to flow, i.e. to pass each other. The close proximity of the chains introduces very powerful cohesive forces which must also be overcome before flow becomes possible.

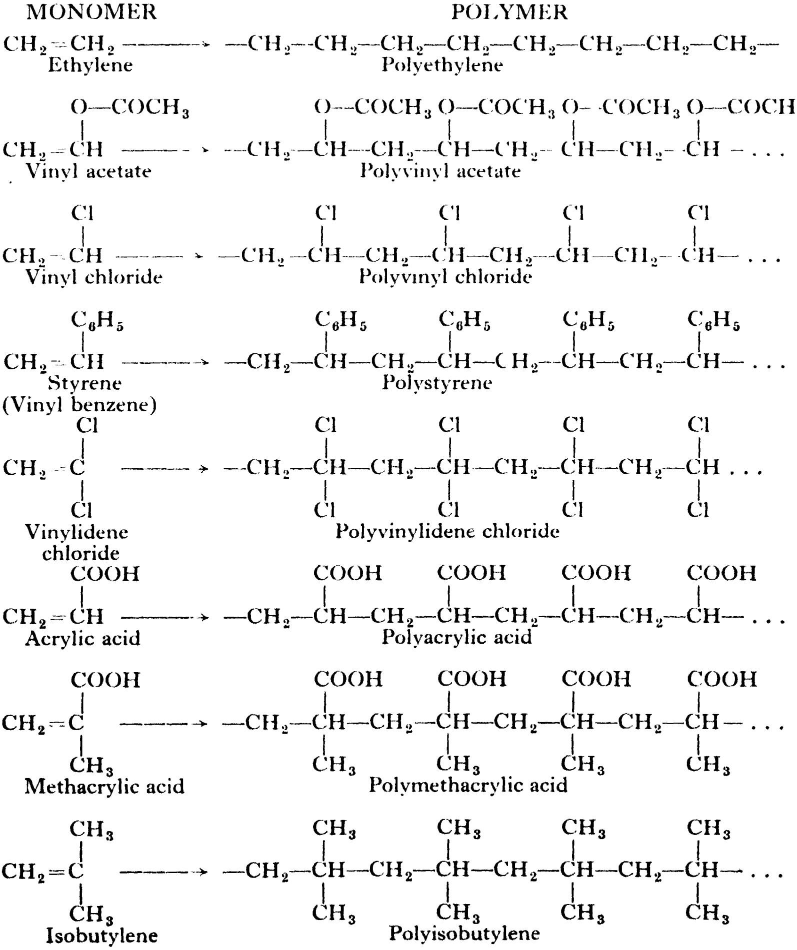
Consideration of a solid plastic made up of long linear molecules implies a number of these molecules in close proximity interlocked at random in every direction, all having a certain amount of liberty of movement, but very restricted. They are tightly packed together, but not so tightly as to prevent them loosening under comparatively low heat, enabling them to slide over each other under pressure to take up a new form which remains solid when cooled. In other words, they are plastic. The development of active plastic characteristics is implied in the action of separating these long chain molecules and permitting them to move past each other. The lines would have to be separated or distanced for easy passing. This could be done by interposing some barrier.

Where the individual units are comparatively simple, and have no bulky appendages attached in the form of side chains, etc., this separation may not be too difficult; for example, in the case of polythene. In many instances, however, there are bulky or lengthy side chains, a notable example is in the case of polystyrene, where there is a large flat benzene ring sticking out from the side chains at regular intervals. Flat plates from adjacent chains may interlock like a "zip fastener" and provide serious steric hindrance—serious obstruction to motion.

The Action of Thermoplastics when Stretched. Yarsley and Couzens[17] have admirably described this: "What happens, then, when a strip of thermoplastic material is stretched? At first the bundles or tangles of threads move slightly from the position which they have taken up as a result of the interaction of the forces acting upon their long constituent chains. They separate from one another against these cohesional forces, and as long as the pull has not been greater than the cohesional force they move back when the force is removed. This corresponds to elastic stretching. As soon, however, as the pull exceeds the cohesional force, which it does at the 'yield point,' the long chains begin to slide one over another, increasing the length of the strip as the pull continues, until the continued sliding of the chains brings enough

TABLE 28

MONOFUNCTIONAL MONOMERS AND THEIR POLYMERS



MONOMER POLYMER

$$CH_2=CH_2 \longrightarrow -CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

Ethylene — Polyethylene

$$CH_2=\overset{\overset{O-COCH_3}{|}}{CH} \longrightarrow -CH_2-\overset{\overset{O-COCH_3}{|}}{CH}-CH_2-\overset{\overset{O-COCH_3}{|}}{CH}-CH_2-\overset{\overset{O-COCH_3}{|}}{CH}-CH_2-\overset{\overset{O-COCH_3}{|}}{CH}-\ldots$$

Vinyl acetate — Polyvinyl acetate

$$CH_2=\overset{\overset{Cl}{|}}{CH} \longrightarrow -CH_2-\overset{\overset{Cl}{|}}{CH}-CH_2-\overset{\overset{Cl}{|}}{CH}-CH_2-\overset{\overset{Cl}{|}}{CH}-CH_2-\overset{\overset{Cl}{|}}{CH}-\ldots$$

Vinyl chloride — Polyvinyl chloride

$$CH_2=\overset{\overset{C_6H_5}{|}}{CH} \longrightarrow -CH_2-\overset{\overset{C_6H_5}{|}}{CH}-CH_2-\overset{\overset{C_6H_5}{|}}{CH}-CH_2-\overset{\overset{C_6H_5}{|}}{CH}-CH_2-\overset{\overset{C_6H_5}{|}}{CH}-\ldots$$

Styrene (Vinyl benzene) — Polystyrene

$$CH_2=\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}} \longrightarrow -CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{CH}}-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{CH}}-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{CH}}-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{CH}}\ldots$$

Vinylidene chloride — Polyvinylidene chloride

$$CH_2=\overset{\overset{COOH}{|}}{CH} \longrightarrow -CH_2-\overset{\overset{COOH}{|}}{CH}-CH_2-\overset{\overset{COOH}{|}}{CH}-CH_2-\overset{\overset{COOH}{|}}{CH}-CH_2-\overset{\overset{COOH}{|}}{CH}-\ldots$$

Acrylic acid — Polyacrylic acid

$$CH_2=\underset{\underset{CH_3}{|}}{\overset{\overset{COOH}{|}}{C}} \longrightarrow -CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{COOH}{|}}{CH}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{COOH}{|}}{CH}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{COOH}{|}}{CH}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{COOH}{|}}{CH}}-\ldots$$

Methacrylic acid — Polymethacrylic acid

$$CH_2=\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \longrightarrow -CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}}-\ldots$$

Isobutylene — Polyisobutylene

chain-ends in a line across the strip to cause a weak place, when the strip breaks."

There is great weight of evidence that many polymers such as polyethylene, polyisobutylene, polyvinyl chloride, polyacrylic esters, polystyrene, polyvinyl acetate, etc., have these long-chain thread-like molecules, especially when they have been produced at low temperatures. A feature of many of these linear high polymers is that when subjected to stretch, numbers of them come into line, and when examined by X-rays, give a regular lattice indicating the formation of crystal structure.

However, most organic thermoplastics ordinarily exist in an amorphous condition, and do not show crystallinity. Polyvinylidene chloride is an outstanding example of the exception to the rule.

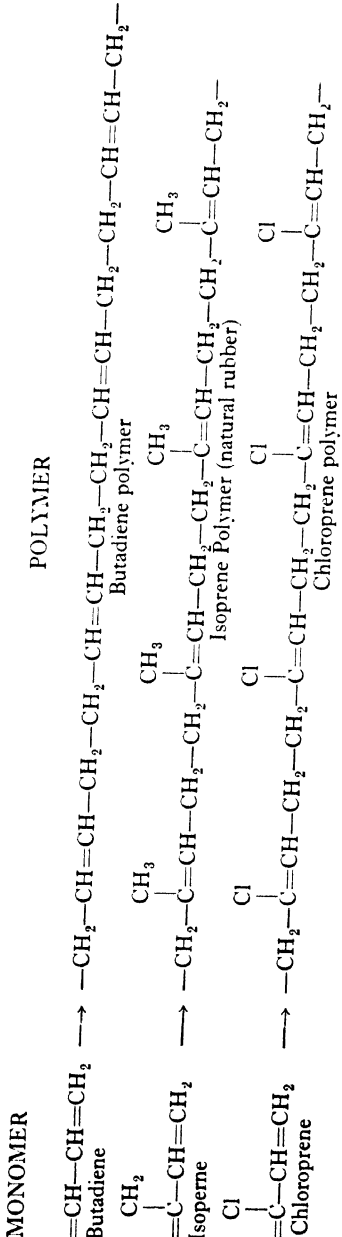
It is generally considered that in the production of synthetic high polymers the straightforward chain polymers are predominantly formed in those cases where the monomeric material contains only one polymerisable group, i.e. a double or triple bond. Outstanding examples of such monomers are vinyl chloride, vinyl acetate, acrylic acid ester, isobutylene, etc. These are the materials which Carothers called *mono-functional.*

In the case of most synthetic rubbers the reacting monomer is one which contains two or more reactive groups, such as butadiene, isoprene, chloroprene, etc. In these cases the formation of two- or three-dimension polymers is not only possible, but usually takes place. These are the monomeric materials which Carothers called bi-functional, or *multi-functional.*

Variations in Polymer Growth. There can be many variations on the main themes. These will depend on the nature of the ingredients and the time factor. It is possible to get a rapid linear growth, and then sudden linking-up between adjoining long macromolecules. It is possible that long molecules can link up with just a few joins or bridges, in which case the behaviour of the final material is substantially the same as a thermoplastic. However, the presence of a few cross-links in this way may be adequate to prevent flow at ordinary temperatures, i.e. cold flow, under the influence of its own weight. There can be a rapid formation of many cross-links, in which case a very rigid three-dimensional structure will be built up, and so on.

It is generally accepted that linear thread-like polymers will be thermoplastic and generally soluble in a variety of solvents. Three-dimensional net-like polymers will in general tend to be infusible and insoluble.

With these materials, the conditions are such as will permit the formation of *branched* systems, or of *cross-linked* systems.



$$CH_2{=}CH{-}CH{=}CH_2 \longrightarrow {-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}$$

$$CH_2{=}\overset{\overset{CH_2}{|}}{C}{-}CH{=}CH_2 \longrightarrow {-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_2{-}$$

$$CH_2{=}\overset{\overset{Cl}{|}}{C}{-}CH{=}CH_2 \longrightarrow {-}CH_2{-}\overset{\overset{Cl}{|}}{C}{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{Cl}{|}}{C}{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{Cl}{|}}{C}{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{Cl}{|}}{C}{=}CH{-}CH_2{-}$$

Fig. 21. Bifunctional Monomers and their Polymers

Cross Linking. Many materials, including multi-functional monomers, form linear macromolecules. This means that even after linking up they still have functional points, i.e. active points at regular intervals along the chain. Addition of certain materials result in a link being formed between adjoining linear macromolecules at such active points. It is evident that even a few such bridges will prevent linear molecules from passing each other. In such cases there is little tendency for cold flow to occur. When there are many such linkages, a more rigid three-dimensional structure is set up. In this case a large number of macromolecules become involved.

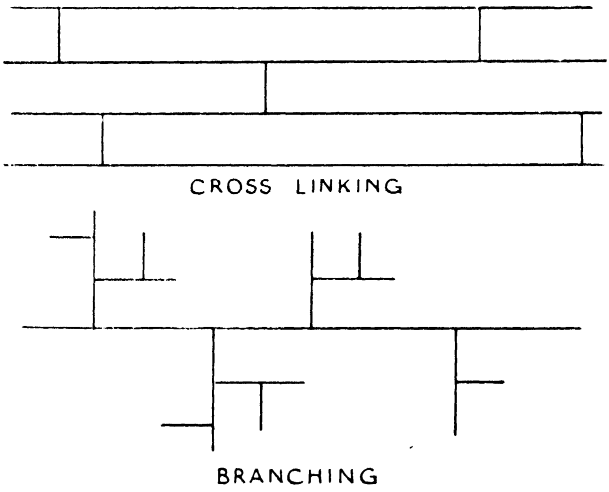


Fig. 22

According to Livingston Smith:[9]

"The existence of a relatively small number of primary links may have an important effect on physical and chemical properties. Thus, if a substantially linear molecule is cross-linked to the extent of 1 in 1,000, solubility is decreased considerably. When the cross-links are individually weak, and all secondary links are much weaker than primary, then the number of links becomes more important. The number of links per chain will clearly depend on the length and orientation of the chains. The more highly oriented the chains, the stronger is the aggregate bond resulting from a number of weak bonds. Another factor of importance is the flexibility of the chains."

Efforts to induce cross-linking probably represent the most important trend at the present time. This appears to be the most favoured angle from which to improve thermoplastic materials.

Branching. In this type of product a linear macromolecule begins to build up. Then a multi-functional molecule joins the chain. The chain thereafter continues to build up from each functional point, branching again each time a multi-functional unit tacks on. A different tree-like three-dimensional structure builds up. In this case a single macromolecule is concerned.

The ability to form gels, or the incidence of gelation, is confined to those polymer systems capable of unlimited growth in three dimensions.

In addition to these types of polymers, there are also those known as net and space polymers, which are two- or three-dimensional. These apply more frequently to thermosetting materials.

The general behaviour of these types of materials show very clearly defined differences. These have been summarised by Mark and Rath.[8] Thus the two- or three-dimensional polymers usually swell to a limited extent and do not go into solution. Examples of these are vulcanised rubber, perbunan, neoprene, etc. They have no definite softening zone of temperatures. They tend to become plastic only at relatively high temperature, and then decompose slowly; a breakdown which is accompanied by increasing plasticity. They exhibit much greater resistance to abrasion and impact and heat than do the long-chain polymers. If there are many cross-linkages, they become brittle and lose their elasticity. They are also found to give very indistinct ring amorphous X-ray diagrams. These have much in common with thermosetting resins, which suggest structural similarities.

In the actual polymerisation there are two main directions for the process. One can either produce straight-chain polymers having free ends, or alternatively cyclised polymers where the ends have come together, while combinations of these are possible. Much of the behaviour of the products, particularly electrical behaviour, will be vested in the free ends of the chains.

It is generally accepted that straight-chain products will process easily, and if subsequent setting is not impeded, then probably such products are most desirable. Cyclised materials are much less readily processed, possibly owing to steric hindrance. In any event, the great problem always confronting the producer is to make the polymerisation process steer a regular well-defined course.

The molecule, according to its make-up, can grow in three dimensions, when a complex net-like structure tends to be built up. This is much more difficult to follow and to study. Thermosetting plastics are considered to behave in this manner.

The Size of Polymers. Plastics may, in general, exist in four different states, namely: (1) the glassy state, (2) the rubber-like (or highly elastic) state, (3) the crystalline state, and (4) the viscous liquid state. In a given material one or more of these states may not occur; thus polymethyl methacrylate does not appear to crystallise under any conditions. Cellulose plastics show marked crystalline behaviour. So do polyvinylidene chloride, nylon, and polythene. The various mechanical properties of plastics are intimately related to the structure of its molecule, and to the arrangement of the molecules in the bulk material.

It is just as well at this stage, in order to get some sort of perspective, to consider the actual dimensions of the molecules and chains which are being discussed. Having talked about long chains and macromolecules and so on, how long are they? Even the longest chains are extremely small. So small that so far measurement has only been possible by means of X-rays in those cases where crystalline structures are formed. In these instances the unit length can be measured. From the molecular weights the approximate chain lengths can be calculated. The following table gives some of the unit lengths:

TABLE 29

	Å
Polyvinyl alcohol	2·52
Polyvinyl chloride	5·0
Polyvinylidene chloride	4·71
Polyethylene	2·53
Polyisobutylene	18·5
Cellulose acetate	10·3
Cellulose nitrate	25·6
Rubber	8·2

These are measured in Ångstrom units, and an Ångstrom unit is 10^{-7} millimetre.

According to Mark,[7] a certain degree of polymerisation is necessary in order to obtain any mechanical strength. This critical minimum is reached by a combination of about 60 to 80 molecules. As soon as this value is surpassed, the material starts to show mechanical strength, which increases proportionally to the average degree of polymerisation. This proportionality holds until the degree of polymerisation reaches about 250. From there on the increase in strength is comparatively small up to a degree of polymerisation of about 700, after which the ultimate strength does not depend appreciably upon chain length.

Two important contributions to our understanding of the behaviour of high polymers have been made in recent years. We can distinguish between typical rubbery, plastic, and fibrous materials. Mark suggests that there is no fundamental difference between these classes but rather a matter of degree concerning the magnitude of the intermolecular forces between the chains and the ease with which they can be fitted into a crystal lattice. Briefly, the state of the high polymer depends on three factors: (1) Entropy (internal free energy, degree of randomness); (2) Molar cohesion (forces between neighbouring chains); (3) Steric factor (bulkiness and restriction of movement). The forces responsible for molar cohesion are van der Waals forces. Where the necessary conditions exist for hydrogen bonds the molar cohesion is particularly strong. Molar cohesion militates towards linearity and crystallinity and so we find that macromolecules with high molar cohesion are normally fibres, e.g. cellulose, polyamides. Counteracting these forces towards linearity is the steric factor, which if large prevents the molecules fitting into a lattice. We, thus, find that polystyrene has a large molar cohesion but nevertheless is not crystalline owing to the bulky nature of the styrene molecule. On the other hand polyethylene is a typically crystalline polymer in spite of its low molar cohesion, because it is particularly easily fitted into a lattice.

The entropy or internal activation likewise opposes an ordered arrangement and so when entropy is increased by increase in temperature, the high-polymer passes through the stages fibre→plastic→ rubber. Plasticisers increase the distance between adjacent chains, decrease the molar cohesion and thereby cause the polymer to be more rubbery. Copolymerisation gives heterogeneous molecules which are even more difficult to fit into a lattice, hence copolymers are usually rubbery. For example Buna/S is more rubbery than either polystyrene or polybutadiene alone.

Turning finally to the question of strength of high polymers, there is found to be a marked discrepancy between the calculated and theoretical values for the tensile strength. Thus the tensile strength of phenol-formaldehyde resin is 7·8 kg/mm.^{2} compared with 4300 kg/mm^2 calculated for primary bonds and 40 kg/mm^2 calculated for secondary bonds. This is put down to "flaws" in the structure or Lockerstellen. The Lockerstellen theory postulates that the maximum theoretical number of primary bonds cannot be formed into a cross-linked polymer owing to the reduced movement and decreased possibility of approach of functional groups as soon as the first links are formed. It is as though the active groups are shielded by the increasing bulk growing round them. The effect is to yield holes in the structure, in which there are free functional groups, and the result is a smaller and weaker macromolecule. For linear molecules, the discrepancy may also be explained by assuming that rupture involves slippage of molecules over one another rather than overcoming primary forces.

Wider Implications of Polymerisation. At one time polymerisation was considered to apply only to systems where monomers, i.e. the single chemical unit, were linked up together, and nothing was eliminated. Polymerisation now has a wider significance, in great part due to the work of Carothers. It is found that some chemicals in themselves will not polymerise or form plastics. But when reacted together they will form new chemical units which can be built up to form long macromolecules. Many other long-chain compounds, having the general properties of polymers, may be formed by condensation reactions in which the elements of some simple compound such as water are eliminated. Only compounds of the first type may be termed polymers in the strict sense in which the term was first introduced. In recent years this narrow interpretation has been discarded. Carothers suggested that the definition of the term polymer should cover all materials containing recurring structural units. Under this definition the polyesters, polyamides, and a large number of other classes of compounds formed by condensation may properly be called polymers. Thus phenol will not polymerise to form a synthetic resin, nor will formaldehyde alone. Yet brought together they will form phenol-formaldehyde resin, one of the most important plastic structures.

Condensation Process. In these condensation processes, there is more than one chemical entity involved—generally two. There is an intermediate step before a reactive unit is formed, such as can be built up into a structure. This usually involves a chemical reaction in which a small molecule (often water) is eliminated. For this reason it is known as a condensation action, i.e. something is squeezed out. Typical examples are phenol and formaldehyde; urea and formaldehyde; glycerine and phthalic anhydride; adipic acid and hexamethylenediamine. Thereafter a larger chemical molecule is formed which is able to grow further into a macromolecule.

There are monomers which can grow simultaneously in three dimensions. For example, butadiene, etc. The essential difference between these monomers when they polymerise, and the condensation systems, is the relationship between *the rate of linear growth* and the *onset of three-dimensional growth.* In most of these monomer systems the growth of the linear molecule goes very far and is the main action. Indeed, it may require some extra effort or some additional promoting material to cause the three-dimensional system to be built up. Until this happens the materials resemble the simple thermoplastic polymers. Typical examples include rubber, polychloroprene, etc. For example, in the case of rubber a promoting material—sulphur—must be present. Bridging can then be induced, for example, by means of heat. In the case of the thermosetting plastics, the linear growth does not proceed very far before the three-dimensional growth begins. This is an over-simplification of the phenomena involved, but it may give some indication of what happens.

The foregoing description shows that it is possible to predict the properties of a material by examining the structure. As a corollary it is possible to prepare materials with desired characteristics by altering the structure along the principles outlined.

Copolymerisation. The polymers formed in the ordinary way have many remarkable properties. There are technical difficulties that limit the wide industrial application of these materials. They are almost invariably thermoplastic in character, sometimes a mixed blessing. In fact, many types of polymers have melting points that are really too low for most commercial applications.

Polystyrene resin has great resistance to moisture, and electrical properties that make it particularly desirable for most electrical applications. Unfortunately it suffers from the severe disadvantage of being somewhat brittle. While various plasticisers to some extent mitigate this difficulty, they also detract from the electrical properties, which fact narrows down any advantage that the plastic may have over other materials, and makes it much less attractive for electrical purposes.

The polyacrylic resins have extraordinary light transmission properties, far transcending those of glass. They also have the unique property of enabling light to travel round curves. But again there is the 'heel of Achilles,' in that they are too soft and scratch easily. This factor prevents a successful utilisation in the field at present almost monopolised by glass. So far no satisfactory solution has been found to this problem.

Polymerised vinyl acetate is not chemically resistant and tends to saponify, which is detrimental for many purposes. And so one may go on finding for each specific type of polymer some defect that acts against its general commercial success. When one comes to the polymers of the butadienes, then totally different difficulties are apparent. They are almost invariably difficult to process and to work, while many of them tend to deteriorate too rapidly.

Examination of the characteristics of many vinyl polymers show quite conclusively that no single one possesses all the properties desirable in a commercial material, such as strength, clarity, stability, water resistance, oil resistance, etc. Yet as a group they have all these properties.

It was soon evident that in many cases, for some specific purpose, the properties of any one polymer might be complementary to those of another. Attempts were made to bring together these polymers with the object of producing a material having almost the ideal properties for the particular purpose. One form which these efforts have taken was to mix the respective polymers together mechanically where possible; another angle was to take them up in solvents and to mix them. Unfortunately, such methods have rarely worked. Almost invariably the result has been to produce a material which is not homogeneous and in which the unsatisfactory characteristics of each polymer have predominated. Outstanding examples of such failures are in connection with rubber, with which many of these polymers have been mixed, nearly always giving useless products.

But in recent years a new technique has been evolved which not only goes far towards solving the problem, but has opened up further new fields for materials capable of polymerisation. Instead of mixing the polymers, the original monomeric substances are brought together and are then polymerised to the desired degree.

The process of copolymerisation is one of the most important in plastics technology. By its means profound modification of the properties of the available vinyl polymers becomes possible. Boyer[2] has compared it with the preparation of metallic alloys. It has already helped to produce materials which possess properties akin to those of the thermosetting resins on the one hand, and to rubber on the other. Only the fringe of the subject has as yet been explored. It seems highly probable that the extended use of the copolymerisation method will facilitate the production of plastics having precisely those properties which changing industrial requirements demand.

The process may be carried out upon mixtures of the monomers as they are, or in solution, or as emulsions. The method employed, however, has a profound influence on the properties of the product.

At first sight it would appear that a mixture of the two separate polymer types would be formed. Actually this is not the case. Entirely new materials result, in which both monomeric groupings are found in the same polymerised molecule.

The properties of the material are different from those which might be anticipated. They are not intermediate between the two types. Generally they are much improved, while there are certain new characteristics that are of great value. Whereas with mechanically mixed polymers the individual ingredients may be separated, for example, by the use of solvents, yet in the case of copolymers such a separation is not possible. The solubility of a copolymer may be very different from those of the components. Thus while vinyl acetate and vinyl chloracetate each polymerise to give soluble products, the copolymer is virtually insoluble in the same solvents.

The Outstanding Copolymer. The outstanding commercial plastic material made by this process of copolymerisation is the product obtained from vinyl chloride and vinyl acetate. Consideration of what happens in this case admirably illustrates the effects of copolymerisation.

Vinyl acetate polymerises to give polyvinyl acetate. This is quite useful commercially and is widely employed as an adhesive. It softens between 30°C. to 40°C. It is exceptionally resistant to heat and light. Owing to the low softening temperature it cannot be processed and moulded with any ease. It also has a relatively high water absorption. A typical ester, it is fairly active chemically; for example, undergoing saponification in the presence of alkalis. It is soluble in alcohols, ketones, esters, chlorinated hydrocarbons, and aromatic hydrocarbons.

Polyvinyl chloride is quite different. It has a very high softening point and is not very thermoplastic. It is chemically inert, virtually non-inflammable, tasteless and odourless. It has great resistance to corrosion, not being attacked even by acids such as sulphuric, nitric, and hydrochloric, nor is it affected by alkalis. It has extremely low water absorption.

Furthermore, it is almost insoluble in all solvents in the cold, although it goes up fairly readily in hot chlorinated hydrocarbons such as ethylene dichloride. It is not particularly stable to light and heat. Because of the high softening temperature and insufficient plasticity, it cannot be processed very easily, so that milling and moulding are difficult. The result is that moulded products have unsatisfactory mechanical characteristics, since all sorts of unrelieved strains are set up which affect tensile strength and impact strength adversely.

Consideration of the properties of these two vinyl compounds showed that if they could be combined a useful material should be obtained. Mechanical admixture of polyvinyl acetate and polyvinyl chloride was tried from every conceivable angle. The resulting mixtures were invariably too weak and brittle. Finally the idea of mixing the monomeric vinyl acetate and vinyl chloride first and then polymerising the two together solved the problem. A copolymer was obtained which consisted of a linear chain molecule in which vinyl chloride and vinyl acetate have reacted with each other, and at the same time have polymerised. The molecule is thought to be as shown in Fig. 23.

The copolymers formed in this way are found to be thermoplastic, odourless, tasteless, and non-inflammable. The mechanical properties are considerably higher than could have been forecast. Not only is the tensile strength very high, but the products are extremely tough and have a measure of resilience. The electrical properties are very good. The materials withstand moisture. The resistance to corrosion and chemical attack is outstanding, while the products are unaffected by soaps, acids, alkalis, oils, and alcohol.

The scope of the copolymer is extremely wide, for it is most versatile and can be worked or moulded without difficulty on rubber or plastics machinery.

The properties of any particular copolymer depend upon the molecular weight (or, in other words, the degree of polymerisation), upon the ratio of the two polymers, and upon their distribution along the chain. The latter factor in turn depends upon the method of production.

The actual distribution of the respective vinyl components along the copolymer chain is a matter of some uncertainty. It can be controlled within reasonable limits only by maintaining rigid control of the conditions under which the polymerisation is carried out. Any deviations may lead to the production of products having different properties. Since the molecular chains may contain some hundreds of the monomer units joined together, there is evidently some scope for variation in the positions. It is these factors which make rather difficult the reproduction of successive batches so as to have absolutely identical properties.

In general, it has been found that the mechanical properties improve with a rise in the degree of polymerisation, while the other properties are more or less independent of this, being rather a function of the chemical composition.

The explanation of the action of the second monomer in copolymerisation appears to be fairly simple. Consider the case of vinyl chloride and vinyl acetate. Polyvinyl chloride is thought to consist of a chain of vinyl chloride units linked together. Sticking out from the chain at intervals are the comparatively compact chlorine atoms. This implies that adjoining chains can get very close together and develop extremely strong forces of cohesion. As a consequence the flow characteristics of polyvinyl chloride are comparatively poor. The adjoining long chains cannot be easily unmeshed—they will not readily push apart and flow.

By contrast vinyl acetate when it appears at intervals in the chains has the comparatively long acetate group sticking out. This effectively acts as a spacer and keeps adjoining chains a fair distance apart which accordingly facilitates flow and gives a more amenable material.

Commercial Copolymers. The vinyl chloride-vinyl acetate copolymer is the example which up to the present has found most use as a commercial material. A number of proprietary products based on this are available. Thus Vinylite, made by the Carbide and Carbon

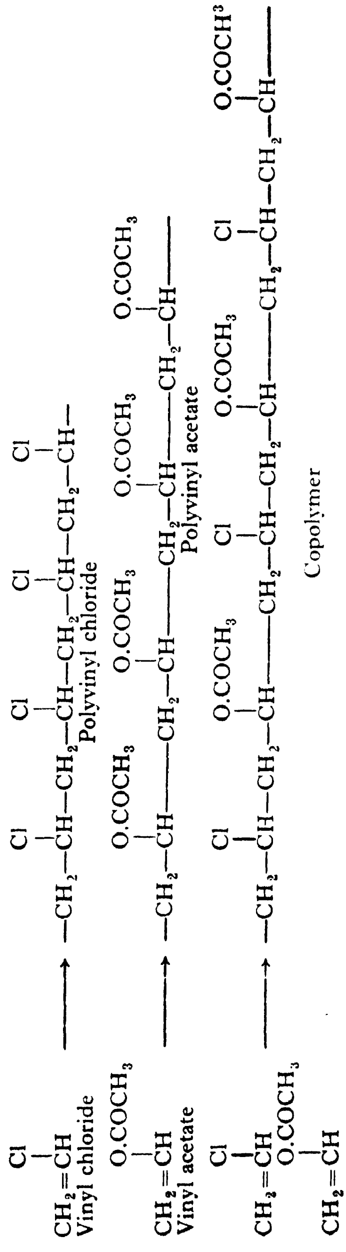


Fig. 23. Copolymerisation of vinyl chloride and vinyl acetate

Chemicals Corporation in the United States, is the proprietary term for a group of such copolymers.

In Germany the I.G. Farbenindustrie make Igelite P.C.U. (*polyvinyl chlorid ungemischt*), which is further compounded to yield the material known as Mipolam. Another Igelite, M.P. (*mischt polymerisiert*) is a copolymer of vinyl chloride and an acrylic acid ester.

The number of these materials is growing rapidly, since they have so many commercial applications.

Another outstanding example of copolymerisation is in the case of polyvinylidene chloride. This material ordinarily has a high softening temperature 185–200° C., which is close to the decomposition temperature, 225° C. It cannot be processed along normal lines. But it copolymerises readily with vinyl chloride. The chief copolymers have softening points from 120° C. to 140° C., and can be handled. These are the "Saran" products made by the Dow Company. Vinylidene chloride also copolymerises with vinyl acetate, styrene, acrylic esters, and many others.

Polyvinylidene chloride is crystalline. Copolymers with less than 70 per cent polyvinylidene chloride are no longer crystalline. The softening point becomes lower as a copolymer is introduced and the material becomes more soluble in solvents.

Copolymerisation and Synthetic Rubbers. There has been great activity in the production of synthetic rubbers and similar materials by copolymerisation of butadiene and other compounds.

Synthetic rubbers made by straightforward polymerisation have been found to have very marked limitations. By forming copolymers, each product possesses the general rubbery properties, but some extra specialised characteristic in addition.

These are well illustrated by the different types of synthetic rubbers. The early types were based on direct polymerisation of butadiene, isoprene, etc., and were found to be unsatisfactory in many respects. The copolymerisation process has facilitated the production of successful materials, having properties which are specially suited for definite applications.

Thus one type, GRS, is a copolymer of butadiene and styrene. Perbunan is a copolymer of butadiene and acrylic acid nitrile. Apart from possessing general rubbery properties, they have special ones. Thus GRS is recommended for electrical resistance, Perbunan for oil resistance, and still another type where heat resistance is required. The production of these copolymer synthetic rubbers proceeds apace; new types are being developed almost daily, although naturally most are found not to be suitable for commercial purposes.

The Process is Specific. The process of copolymerisation is specific. That is to say, it does not follow that admixture of any two vinyl monomers will inevitably produce a copolymer. For example, styrene and vinyl acetate will not polymerise together. All that happens is that the styrene polymerises in the normal way to yield polystyrene, while the vinyl acetate remains unchanged. The nature of the radical attached to the parent nucleus has a profound bearing on this ability to yield copolymers.

Methods have been developed which have overcome to a great extent this reluctance of some monomers to copolymerise. In fact the I.G.[5] claimed to be able to copolymerise any pair of the vinyl and acrylic acid series. Röhm and Haas[12] likewise make a similar claim for different members of the methacrylic series of compounds. According to another patent the I.G. claimed that mixtures of such monomers which in the normal way will not copolymerise could be made to do so by means of suitable promoting agents. Their method was extremely ingenious. They added substances which readily copolymerised with either of the components of the mixture. Thus styrene and vinyl acetate, which, as already stated, do not copolymerise in the ordinary way, did so in the presence of acrylic acid and esters. Styrene and vinyl chloride were made to copolymerise by the presence of maleic acid esters. In some cases even a fourth component could be added. The proportions of the materials could be varied within very wide limits.

Developments of Copolymerisation. Another aspect of copolymerisation, although known for some years, is only now beginning to acquire commercial importance. It was found possible for certain types of materials which in the normal way were not known to polymerise to enter into copolymers with suitable polymerisable compounds. Thus maleic acid derivatives are not ordinarily known to give polymers. The molecules are unable to link up together. Yet maleic anhydride will form copolymers with styrene under suitable conditions. Apparently the styrene is able to take it up during polymerisation, since the maleic-anhydride appears in the final molecules.

Yet there is some law that controls this action, for it is found that when excess of styrene is present all of this will go into the polymers with the maleic acid anhydride. With excess of the latter it is found that only the chemical equivalent will go into the copolymer, the remainder remaining unchanged.

Solubility and Thermoplasticity. Another important aspect of copolymerisation has yet to be considered.

It has recently been shown that by utilising small quantities of specially selected secondary materials that it is possible completely to modify characteristic properties of the polymers. Thus the introduction of small amounts of divinyl compounds to ordinary vinyl materials is found to give insoluble polymers by contrast to the polymerised vinyl compound which is soluble in the solvent in question. It is considered that these additions give the long-chain molecules a very pronounced three-dimensional character. This procedure has acquired some commercial significance.

Staudinger and Heuer[14] showed that additions of small amounts of divinyl-benzene to styrene yielded, after polymerisation, an insoluble polymer which would only swell to a limited extent in solvents in which polystyrene is freely soluble.

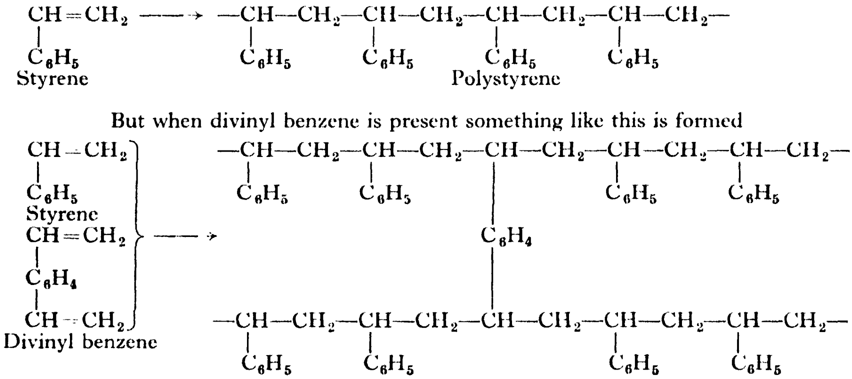


FIG. 24

This was thought to operate because the divinyl benzene caused the normally unbroken straight chain of polystyrene to branch when one of these molecules joined in. Each branch would proceed from a certain length and would again pick up a divinyl benzene molecule and would branch again. In this way a three-dimensional structure is rapidly built up, a fact which is considered to modify profoundly the behaviour of materials in solvents. It only needs comparatively few molecules of the divinyl compound to exert a very marked effect. This principle of adding a small amount of a multi-functional material is being widely applied to modify the character of substantially linear macromolecules.

Blaikie and Crozier[1] described how, by forming a copolymer of vinyl acetate with a small amount of divinyl ether, a material was obtained that was quite different from polyvinyl acetate in that it was quite insoluble in solvents for this polymer.

Other materials known to exert this insolubilising effect in vinyl derivatives include glycol diacrylate and hydroquinone diacrylate.

Dorrer, Hopff, and Staudinger[4] polymerised aliphatic vinyl compounds such as aliphatic vinyl esters or ethers in the presence of 5 per cent of divinyl benzene or isopropenyl benzene. The resulting materials were completely insoluble in aromatic hydrocarbons, although some did swell to a slight extent.

Modification of the polymerised materials is tackled from two directions. The one that has already been discussed is regarded to function by introducing materials into the straight-chain molecule that will cause the chain to acquire branches, so that a single straight chain becomes tree-like, spreading into a third dimension, causing molecular obstruction in solution.

Another angle that is being attacked is to introduce into this molecule another material which, although able to copolymerise, still retains part of its unsaturated nature, so that the copolymer itself is still chemically reactive. This procedure has been particularly aimed at overcoming the thermoplasticity of these plastics, a factor which is frequently a disadvantage. Thus the I.G.[5] proposed to overcome this disadvantage by copolymerising the vinyl compounds together with another vinyl compound which, in addition to the vinyl grouping, contained another unsaturated aliphatic group, the latter not being affected by the polymerisation process yet able to make the material vulcanisable. They formed a copolymer of acrylic acid ethyl ester and a dimethyl acrylic acid vinyl ester.

Staudinger[15] has described the parts played by the chemical structure and the physical arrangement. He says: "Chemical structure, together with physical arrangement of the polymer molecule, can be used to explain nearly all characteristics of these macromolecules. Dealing first with the chemical constitution, one can say that generally the chemical behaviour is influenced mainly by the constitution and the nature of the end-groups and that of the secondary, or side groups, which are attached to the main chain, while the physical properties are also influenced by the length of the chain and its degree of attachment by cohesional forces to adjoining chains; for example, the physical properties, which are markedly dependent on the length of a chain molecule, are the nature of its solution, and the tensile strength, while plasticity and elasticity derive their variation also from differences in the constitution of the secondary groups and from the configuration of the polymer.

REFERENCES

1 Blaikie and Crozier. *Ind. Eng. Chem.*, 1936, **28**, 1158.
2 Boyer. *Modern Plastics*, 1943, June, p. 62.
3 Carothers. *Trans. Far. Soc.*, 1936, **32**, 41.

4 DORRER, HOPFF AND STAUDINGER. G.P. 652,276.

5 I.G. B.P. 468,084/1936, B.P. 498,329/1938.

6 MARK. "*Der Aufbau der hochpolymeren organischen Naturstoffe*," Leipzig, 1930.

7 MARK. *Ind. Eng. Chem.*, 1942, **34**, 11.

8 MARK AND RATH. "*High Polymer Reactions*," New York, 1941, p. 81.

9 LIVINGSTON SMITH. *British Plastics*, 1943, **15**, 391.

10 MARVEL. *J. Amer. Chem. Soc.*, 1930, **52**, 376 *et seq.*

11 MELVILLE. *Proc. Roy. Soc.*, 1937, A.163, 511.

12 Röhm and Haas Corp. B.P. 467,402/1936.

13 STAUDINGER. "*Die hochmolekularen organischen Verbindungen*," Berlin, 1932.

14 STAUDINGER AND HEUER. *Ber.*, 1934, **67**, 1164.

15 STAUDINGER, H. P. *Trans. I.P.I.*, 1943, **11**, 41.

16 WHITBY. *Trans. I.P.I.*, 1930, **5**, 184.

17 YARSLEY AND COUZENS. "*Plastics*," Penguin, London, 1941, p. 33.

PART II

THERMOSETTING RESINS AND THEIR PLASTICS

CHAPTER IV

PHENOLIC RESINS

THE phenol-formaldehyde class of resins, also referred to as the phenolic resins, is the most important group of plastic materials at the present time. Until comparatively recently there was no questioning its supremacy. Now several other types of plastics are gaining rapidly in volume, and may in due course surpass it. It is a question of speed of development. While phenol-formaldehyde still progresses at what ordinarily seems a rapid rate, some others are expanding in a phenomenal manner. However, in 1947 consumption of phenolic resins exceeded 300 million pounds.

The chief raw materials are formaldehyde and phenol, or cresol. The latter is mainly meta-cresol with minor amounts of ortho- and para-cresol present.

Apart from these, other chemicals which have phenolic groups, such as xylenol, resorcinol, and so on, give commercial resins. On the other hand, aldehydes other than formaldehydes may be used. However, as a rule the simple chemicals are more readily available and predominate.

Historical Background. Phenol-formaldehyde resin was the first commercial synthetic resin to be made, having been described and patented in 1908 by Baekeland.[2] It is still the most versatile of all known synthetic resins, and is produced on an ever-growing scale.

Nevertheless, the history of phenol-formaldehyde dates from long before this time. Baeyer[4] in 1872 noted that phenols and aldehydes reacted to give resinous products. The reaction was not specific to this pair, i.e. phenol and formaldehyde, but was general. However, until the advent of Baekeland the reaction could not be brought under control. In the interim a considerable amount of work was carried out in the field of phenol-formaldehyde resins. For example, Kleeberg[7] found that formaldehyde reacted with phenol, resorcinol, pyrogallol, etc., in the presence of concentrated hydrochloric acid to give resinous or viscous insoluble products.

In 1900 Smith[20] had prepared resins from phenol and paraldehyde.

He obtained a useful material which could be moulded and he proposed to utilise this for electrical insulation. Shortly after this there was an active interest in developing substitute materials for shellac, which was then in short supply. This stimulated great activity with the resins obtained from phenol and formaldehyde.

Luft[10] employed acid catalysts, such as hydrochloric or oxalic acid, in the reaction, to prepare resinous materials which he found to be soluble in acetone and alkali. He proposed to add fillers to this material, and to use the products for making moulded articles.

A few years later Story[21] prepared viscous materials by heating phenol with formaldehyde at high temperature for a number of hours. He cast this material in moulds and hardened it by heating at temperatures below 100° C. for some time. A hard, tough, transparent, insulating material was obtained. This was the forerunner of modern cast phenolic resins. He also found that the resinous materials could be dissolved in solvents to give a product which could be employed as a varnish. Due largely to the lack of uniformity these products did not achieve much success. For one thing, the copious evolution of gases during the hardening process led to useless products.

A considerable amount of useful work was carried out in this field by Lebach,[9] who prepared phenol-formaldehyde resins, employing organic acid chlorides and aluminium chloride as the condensing agent.

Arrival of Baekeland. This was followed by the classical work carried out by Baekeland[2] which first established satisfactory procedure in controlling the reaction between phenol and formaldehyde. He worked out all the necessary conditions required to maintain this control. In 1908 he was granted the patent, in which it was shown that a resin which could be hardened by heat was produced by using an alkaline catalyst to the extent of 0·5 up to 10 per cent, which is equivalent to one-fifth of the proportion of phenol present. He stressed the point that in no case should this exceed 20 per cent of the total reaction mixture. He also showed that porosity could be overcome by carrying out the heating under high pressure.

A short time afterwards came the patent which illustrated the technique for converting the resin by a short moulding process into a moulded article having excellent mechanical and electrical characteristics.

Rapidly following on these developments came patents for preparing solutions of the resin and using such solutions in impregnating fibrous sheets for the preparation of laminated materials.

The master patents expired in 1926, and thereafter there was a considerable expansion in the number of concerns interested. This accounts for the numerous proprietary types now available.

Leading Raw Materials—Phenol. As has already been suggested, phenol is the prototype of a large group of phenolic materials which are capable of forming useful synthetic resins with aldehydes. By far the most important commercially are phenol itself, and the cresols. There is a host of substituted phenols which also form resins. In many instances they are oil-soluble and these have a limited, if important, use.

Phenol or carbolic acid (molecular weight 94) is a white crystalline compound, which turns pink on exposure to air. Commercial phenol as used in present-day manufacture is 99·7 per cent pure, and melts at 40·8° C. It has always been obtained as a by-product in the distillation of coal-tar; but the demand for phenol has been so great that coal-tar as the sole source of supply has become utterly inadequate. As a result, in recent years the synthetic production of phenol has made enormous strides.

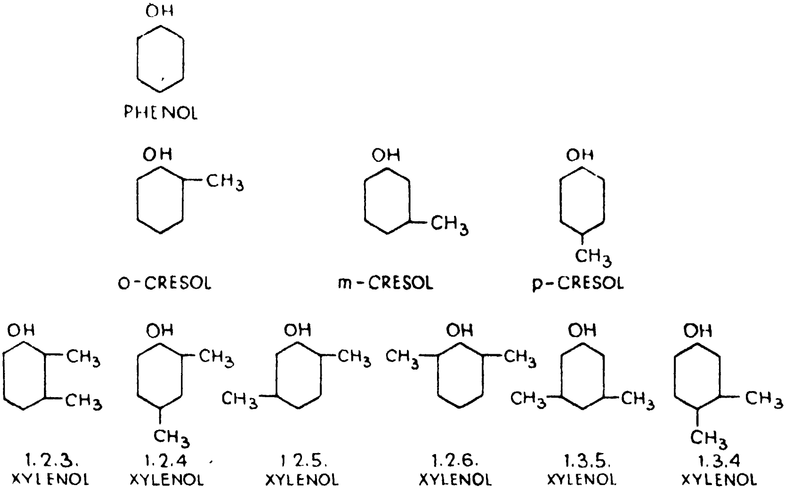


Fig. 25. Typical phenols used for making resins

In the distillation of coal-tar the fraction following phenol is cresylic acid, or cresol (molecular weight 108) obtained as a light brown liquid. There are invariably three isomers of cresol present:

Ortho-cresol: melting at 31°C.; boiling point 191°C.
Meta-cresol: melting at 12°C.; boiling point 205°C.
Para-cresol: melting at 34·7°C.; boiling point 202°C.

They differ only slightly in their physical properties. In their chemical behaviour, particularly where resins are concerned, they differ considerably. Meta-cresol is by far the most important of the three; it reacts readily with formaldehyde, giving a fast-setting resin. Thus, in order to obtain satisfactory synthetic resins, the proportion of meta-cresol must be greater than 55 per cent, while the amount of o-cresol must not exceed 5 per cent. The specific gravity should be 1·036. Owing to the cost comparatively little has been done about separating them, so that the composition as obtained from coal-tar is very important.

Such mixed cresols are far cheaper than phenol. Ordinarily there is a very ready supply of them. Since they give extremely satisfactory moulding resins, albeit somewhat dark in colour, they are in great demand. So much so, that since the U.S. coal-tar industry cannot adequately supply their plastics industry with cresylic acids, large quantities are imported from Great Britain.

As an indication of quantities involved, the following U.S. particulars are extremely enlightening:

TABLE 30

UNITED STATES PRODUCTION AND SALES OF PHENOL IN THOUSANDS OF POUNDS[22]

Year	Production	Sales	
		Quantity	Unit Value
1917	64,147	64,147	$·37
1918	106,794	106,794	·35
1919	1,544	1,544	·10
1923	3,311	2,180	·27
1925	14,734	8,524	·21
1926	8,691	5,480	·18
1927	8,041	4,595	·15
1928	10,277	7,746	·12
1929	24,178	19,939	·11
1930	21,147	17,715	·11
1931	17,981	14,002	·10
1932	13,965	12,181	·10
1933	33,220	27,923	·10
1934	44,935	36,241	·11
1935	43,419	34,575	·10
1936	48,724	40,942	·10
1937	65,690	57,176	·11
1938	44,548	32,196	·11
1939	68,577	59,857	·10
1940	96,155	—	·09
1941	130,000	—	—
1948	239,000	—	—

Present U.S. annual production of phenol exceeds 200,000,000 lb., of which about 86 per cent is synthetic and 14 per cent is natural. About 55 per cent of the total goes into plastics. So far as the coal-tar industry is concerned, here are some figures for 1947:

TABLE 31

USES FOR PHENOLIC RESINS[23]

Tar Acid Resin Production, U.S., 1947, in lb.

Total Usage	252,000,000
For Adhesives	32,000,000
For Laminating	40,000,000
For Moulding and Casting . .	115,000,000
For Protective Coatings . . .	31,000,000
Other Uses	34,000,000

Synthetic phenol is made in this country by the Monsanto Company Ltd. In the United States a number of concerns are interested. Among the most important are Barrett, Dow, Durez, and Monsanto. Du Ponts are also extremely active, but their synthetic phenol is not used for phenolic resins, but for adipic acid, as an intermediate in the production of nylon. Several other large concerns, including G.E.C., of America, are constructing synthetic phenol plants.

Synthetic Production of Phenol. The synthetic production of phenol is carried out along the following lines.[13] Commercial synthesis of phenol involves the conversion of benzene in two stages as:

$$C_6H_6 \longrightarrow C_6H_5X \longrightarrow C_6H_5OH$$

Where *X* may be either the SO_3H- group (sulphonation method) or Cl (halogenation method).

Considering first the sulphonation method the reaction

$$C_6H_6+H_2SO_4 \longrightarrow C_6H_5SO_3H+H_2O$$

will only go to completion if one of the products is removed as follows:

(*a*) Water as hydrates of sulphuric acid.
(*b*) Water by distillation.
(*c*) Benzene sulphonic acid.

One process removes the benzene-sulphonic acid as a 2 per cent solution in benzene, and can be made continuous. This is considered to be the most efficient of the sulphonation processes, but it requires large-scale installation and efficient benzene recovery, since 49 lb. of benzene must be used for each pound of benzene-sulphonic acid produced. Furthermore, the same quantity of sulphuric acid must be cycled as in the excess acid method although the spent acid may be reconcentrated.

All sulphonation methods require conversion of the benzene sulphonic acid to the sodium salt (by means of soda ash or by-product sodium sulphite) and evaporation to dryness before fusion. In this operation, about 2·5 to 3 mols (25 to 50 per cent excess) of fused caustic soda are used per mol of sodium benzene sulphonic acid, with about 10 to 20 per cent weight of water, fusion occurring at about 300° C. Open hemispherical iron pots with agitators are employed; and about 9 hours are required for a 1,500 lb. batch of phenol. The fusion mass is discharged into a measured quantity of water when phenol may be liberated by acidification. It is then recovered by distillation.

The major disadvantages of the fusion process are the large amounts of caustic soda required and the oxidation of sodium phenolate due to contact with air. Maximum yield are about 92 per cent. The best conversion of benzene to phenol works out to about 90 per cent.

In the continuous halogenation process, either alkaline or catalytic hydrolysis is used. In the alkaline process worked by the Dow Company, chlorobenzene, 25 per cent excess sodium carbonate, and water are reacted at 320 to 400° C., and 3,000 lb. per sq. in. pressure to give free phenol in a yield of from 84 to 95 per cent of theory. Diphenyl oxide is a by-product, but its formation is said to be inhibited by including it to the amount of 10 per cent in the reaction charge. In the chlorination of benzene the yield of chlorobenzene is only 70 per cent so that the overall yield of phenol from benzene is only about 66 per cent. The high operating pressures and temperatures, as well as equipment cost, restrict the use of this process to large operations; and markets must be maintained for disposal of the by-products—o- and p-dichlorobenzene and diphenyl oxide.

The Raschig Method. The Raschig[17] process is stated to produce less than one-tenth of a pound of by-product for each pound of phenol.

The Raschig, or regenerative method,[18] is the most recently developed commercial process and is based on the catalytically promoted reactions:

$$C_6H_6+HCl+O \longrightarrow C_6H_5Cl+H_2O$$
$$C_6H_5Cl+H_2O \longrightarrow C_6H_5OH+HCl$$

The process itself is somewhat complicated. Briefly, it consists, first, in passing a vapour mixture of benzene, hydrochloric acid, and air through a catalyst.[16]

Material costs are low; theoretically only benzene and atmospheric oxygen are required. Conversion, however, is also slow. Chlorination is also accomplished with 15–20 per cent hydrochloric acid at 200° to 250°C. In the presence of copper-iron or copper-cobalt catalysts imbedded on activated alumina there is obtained a 12 per cent conversion per pass. This produces a mixture of chlorinated benzenes from which monochlor-benzene is distilled in the pure state for use in the second step. In this second step, a vapour mixture of mono-chlorbenzene and steam is passed through a catalyst which produces phenol and regenerates the hydrochloric acid. The catalyst consists of active silica or phosphates of magnesium, calcium, and zinc at 400° to 500° C. with a 10 per cent conversion per pass. These two stages actually form a completely continuous process, and during the process most of the materials formed, and the catalysts, are recovered for re-use, phenol being extracted or drawn off as it is formed, and new materials and new catalysts added as the original materials wear out or become used up.

Yields are not published but about 3 per cent of hydrochloric acid is lost owing to the formation of higher chlorinated products, while diphenyl oxide is also formed in the hydrolysis step. The important considerations in the successful operation of this method are corrosion and heat recovery.

Formaldehyde. Formaldehyde is a key material for many forms of synthetic resin production. Output amounted in 1948 to about 523,000,000 lb., of which half went into plastics. It is not only of paramount importance for phenolic resins, but the same applies equally to aminoresins, to melamine resins, to polyvinyl formals, and to many other types. It is a fact that formaldehyde appears to be the only aldehyde which gives synthetic resins which will set rapidly enough for present-day requirements.

It is available in three forms:

(*a*) As gas.
(*b*) As a solution of the gas in water known as formalin.
(*c*) As a white solid produced from formalin.

Formaldehyde is a gas at normal temperatures. It is obtained synthetically by the hydrogenation of carbon monoxide. The more usual method is to pass methyl alcohol, which is wood alcohol, as vapour over a heated catalyst, such as copper oxide. The vapours are passed into water, which absorbs them.

A solution containing about 40 per cent formaldehyde is the material known as formalin.

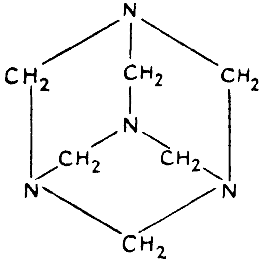
Complete transformation into formaldehyde never occurs, and consequently a little methyl alcohol is always present. A minute amount of formic acid also occurs by oxidation of the formaldehyde. The presence of these materials is not inimical to resin production. The minute amount of formic acid is considered to act as a catalytic agent in the formation of phenolic resins.

Formalin solution, on standing, gradually polymerises and deposits a white solid. This material is a polymer of formaldehyde. The exact nature of the polymer is not yet clear. It reacts in almost the same manner as formaldehyde, but being insoluble in water, and having a high specific gravity, it settles out. This material is known as paraformaldehyde, and when heated it returns to the gaseous condition, i.e. formaldehyde.

Another form in which formaldehyde is obtained for use in the production of phenolic resins is as hexamethylenetetramine. Formaldehyde combines with ammonia with the evolution of heat,

$$6\,HCHO + 4\,NH_3 \longrightarrow (CH_2)_6\,N_4 + 6\,H_2O$$

and from the solution thus formed, a white crystalline material is obtained, known as hexamethylenetetramine, or hexamine. It forms rhombic crystals with melting point of 280° C. The molecular weight is 240 and the specific gravity 1·02. This material readily gives up its formaldehyde, and can be used in the production of synthetic resins. Furthermore, the ammonia is also liberated during the resin production and acts as a very effective catalyst.



Estimation of Formaldehyde Content. The formaldehyde content is estimated in the following manner:

Three c.cs. of the solution are added to 50 c.cs. of solution of hydrogen peroxide, and 50 c.cs. of N sodium hydroxide and warmed on a water bath till effervescence ceases. The excess of alkali is titrated with N sulphuric acid, using phenolphthalein as indicator. A blank test is then done by repeating the operation without the solution of formaldehyde. The difference between the two titrations represents the sodium hydroxide required to neutralise the formic acid produced by the oxidation of the formaldehyde by the peroxide. Each c.c. of N sodium hydroxide is equivalent to ·0300 gm. of formaldehyde.

Petroleum as a Source of Formaldehyde. The petroleum industry is beginning to acquire importance as a source of formaldehyde. This is derived from natural gas, which is of course always found in enormous quantities in the oil fields. Methane is one of the chief constituents of natural gas. It is converted into formaldehyde by air oxidation. The first commercial plant was started in 1938 in the United States.[15] A substantial tonnage of methyl alcohol, acetaldehyde, methyl ketone, etc., is also obtained by partial oxidation. The mixture is separated into the major ingredients by fractionation.

The Preparation of Phenolic Resins. Phenol and formaldehyde condense to form resinous materials. This behaviour is not confined to these two materials. They are representative of types: thus, cresols may be used instead of phenol, while other aldehydes, a notable example being furfural, may be employed in the place of formaldehyde. Good moulding resins are made commercially from phenol, or from m-cresol.

The variety of materials obtained by varying the ingredients is very wide. In addition, different materials may also be obtained by varying the conditions under which they are made.

Fig. 26. Typical resin manufacturing unit

There is much confusion concerning the mechanism of the formation of phenol-formaldehyde resins, and a great deal of controversy. This is due to the fact that there are a number of variable factors. No clear picture has as yet been formulated to assess the relative importance of these factors in relation to the final products. On the one hand there are two sharply defined forms of procedure adopted in the preparation of commercial resins. These are the:

(*a*) *One-Stage Process* where *the whole of the formaldehyde* is added to the phenol at once in the presence of the catalyst.

(*b*) *Two-Stage Process* where *a portion of the formaldehyde* is first added to the phenol, insufficient to produce an infusible and insoluble resin. The balance is added at a later stage altogether with some or all of the catalyst.

This division is further complicated by the question of whether an alkaline catalyst or an acid catalyst is employed. Great emphasis has been laid on each of these factors from time to time.

One-Stage Resins. If molecular equivalents of phenol and formaldehyde are mixed together, and a small amount of sodium hydroxide solution is added, there is a brisk reaction. An alkaline catalyst is usually employed in this method. Thus Baekeland used ammonia which has proved an excellent catalyst. Phenol-formaldehyde resin is rapidly formed.

Preparation of a One-Stage Resin
94 parts phenol.
100 parts formalin.
9·4 parts ·880 ammonia.

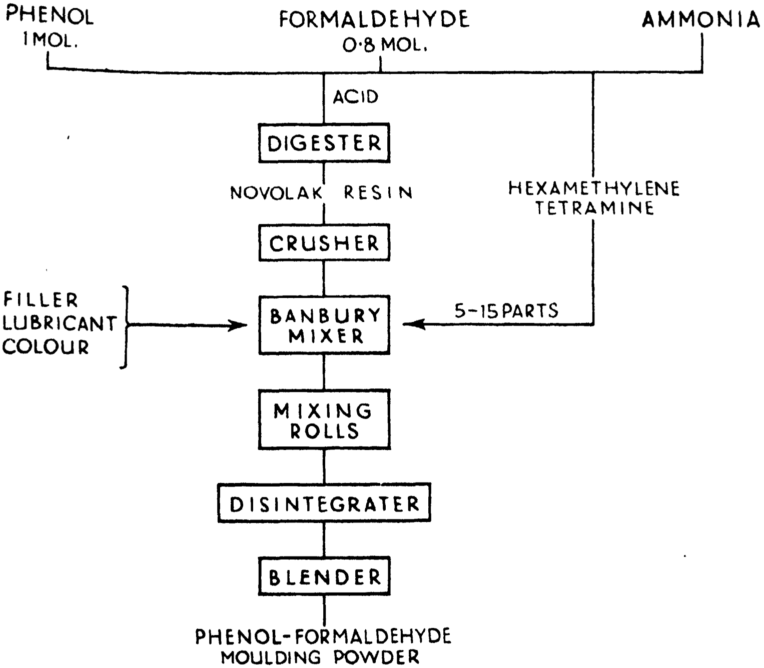


Fig. 27. Flow sheet for a two-stage resin moulding powder

These ingredients are slowly brought to boiling point under reflux. The temperature must be carefully controlled in order to prevent the resin from passing to the infusible condition. Usually water-cooling is employed to keep the temperature below 100° C. After about half an hour there is a separation into two layers. The resin is subjected to vacuum distillation at about 80° C. in order to remove water, and there remains a honey-coloured fluid resin. When this resin has been formed, its subsequent behaviour is found to be entirely dependent upon temperature. At low temperature no further reaction proceeds, whereas if the temperature is raised the resin proceeds towards the end condition.

When cooled this resin becomes a hard brittle solid (specific gravity 1·28) which may be crushed to powder. At this point it is still thermoplastic, but relatively little further heating can cause it to proceed to the final infusible condition. Since there is no known solvent for the set resin, if it does set in the digester it has to be laboriously chipped out. For this reason it is known as a single-stage resin, since the application of a single factor, namely heat, can cause it to become infusible.

The Resins exist in Three Definite Conditions. In actual fact, the honey-coloured resin appears to exist in three clearly defined conditions. As prepared it is soluble in solvents such as alcohol and acetone, and such solutions are the basis of many industrial lacquers, varnishes, impregnating solutions, etc. Baekeland described this material as *Resol* (or Resin A).

Slight heating converts this to the *Resitol* (or Resin B), when it is no longer soluble in the solvents mentioned, but is still thermoplastic. Further application of heat converts it into *Resit* (or Resin C), which is quite infusible and represents the final condition of the resin.

As prepared in the one-stage process, the transition from *Resol* to *Resit* is extremely rapid and critical. Because of this they are not much used for moulding powder, but rather for applications in solution as adhesives for laminating and impregnation and for certain lacquers.

Properties of Resit or Resin C. Phenolic resin in the conditions known as the "C" state, or *Resit*, is unique when compared with any natural resin. Besides resisting temperatures up to 300°C. the resin is strong, possesses good heat and electric insulating properties, is extremely inert, resisting attack by all but the most powerful reagents, and is quite insoluble in all organic solvents. It is even resistant to hydrofluoric acid, which attacks glass, and consequently may be used for constructing containers for that acid.

This end-product *resit*, or resin C, is brilliant, hard, clear resin of high refractive index and pleasing yellow-brown colour, and may be used as a substitute for amber for decorative and utility articles.

Articles such as umbrella-heads, fountain-pens, beads and cigarette-holders can be machined from solid blocks (cast into glass moulds) and polished. By the introduction of waxes and pigments, cloudy and tortoiseshell-like effects may be produced, and by a special method of manufacture the resin may be pulverised and moulded under heat and pressure, still retaining its transparency.

It should be noted that phenolic resins tend to darken on exposure to light and air. As yet, no reliable means has been found to prevent this.

The Two-stage Resin. In order to make commercial moulding powders, a modified procedure is employed which results in resins that are less critical and touchy and more easily handled. These are known as two-stage resins.

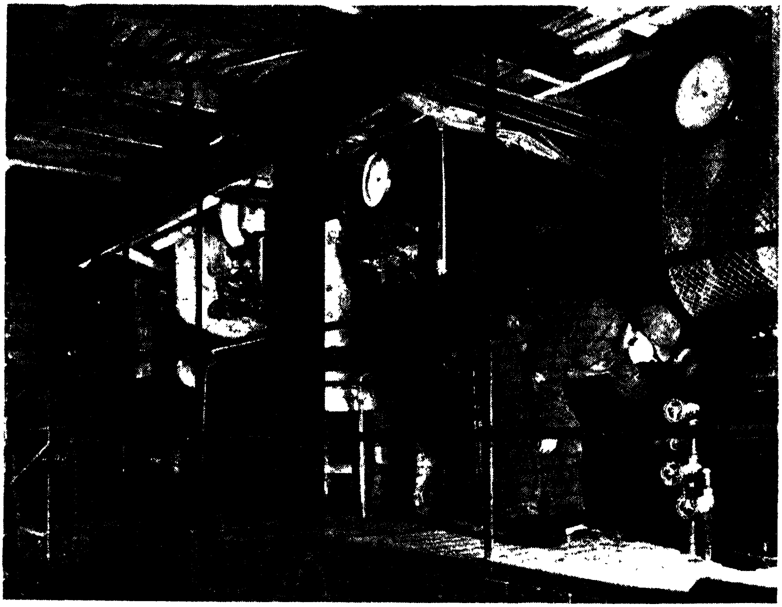


Fig. 28. Some of the reaction vessels for the manufacture of phenol-formaldehyde resin[25]

This type of resin is prepared by reacting phenol with less than the equivalent quantity of formaldehyde in the presence of an acid catalyst. This results in the formation of a resin which is fusible and which cannot be set merely by the application of heat. The resin formed is virtually permanently fusible and is known as *Novolak*, the name given by Baekeland.

In order to enable the resin to proceed to the final *resit* condition, it is necessary to supply a further quantity of formaldehyde in some form. This is generally achieved by the addition of polymers of formaldehyde, such as paraformaldehyde, or more generally by the addition of hexamethylenetetramine. In the latter case between 10–15 per cent is added. This brings the amount of formaldehyde up to 1·5 equivalents

This will transform the resin to a thermosetting type, for which the ammonia, released simultaneously, will act as catalyst. Credit for the initial use of hexamethylenetetramine goes to Aylsworth.[1]

This is the most widely used method for the production of phenol formaldehyde resins for moulding powders. The resins formed can be handled and heated without fear of passing to the set condition. Their use offers many manufacturing advantages. It enables the addition of other essential ingredients without the risk of ruining batches of material.

In actual fact it is not correct to state that these two-stage resins, or novolaks, are permanently fusible. This is only quite true when there is a comparatively small proportion of formaldehyde present.

TABLE 32

SUMMARY OF REACTION TYPES

Phenol	Formaldehyde	Catalyst	Type of Resin
1 mol.	More than 1 mol.	Alkaline	One-step
1 mol.	Less than 1 mol.	Alkaline	Two-step
1 mol.	1 mol.	Acid	Novalak
1 mol.	3 mol.	Alkaline	Cast Resin

The Preparation of Phenol-formaldehyde Resins. The phenol-formaldehyde condensation is carried out in a digester or kettle. Because phenol or cresol is very corrosive, the digester must be specially constructed either of copper or steel, being lined with enamel or with nickel. Some are made of silver or of monel metal. The digester is jacketed, so that it may be steam-heated or water-cooled. It is fitted with stirring gear, and is connected with a vacuum pump. There is a glass viewer through which the progress of the reaction can be studied. A large valve in the bottom serves as an exit for the finished resin. In actual production from time to time samples are removed and tested for free formaldehyde.

The resin is usually poured out of the bottom into large trays to a depth of several inches, cooled, and the solidified resin is broken up by means of sledge-hammers. It does not adhere to the trays.

A very much improved method employs a continuous steel belt which carries away the resin as a relatively thin layer which can easily be reduced to powder form. Prepared in this manner the resin is ready for conversion into moulding powders.

Some Manufacturing Procedures.

A One-Stage Method using Cresol

The following may be taken as an example of a resin made by a wet one-stage process, and suitable for general purposes:

Cresol	500 lb.
Formaldehyde	450 lb.
Sodium hydroxide	2 lb.

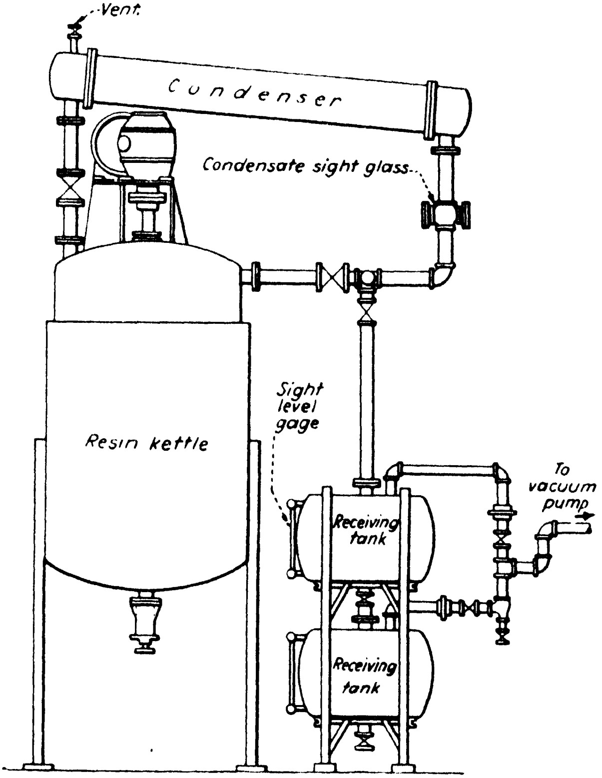


Fig. 29. Typical set-up of resin kettle and accessories

The materials are weighed out and a slight vacuum is applied to the digester, when on opening the feed-cock the mixture is immediately sucked into the interior. The stirrer is started up, revolving at about 40 r.p.m. and the water turned on in the reflux, care being taken to see that all the valves are correctly adjusted.

The contents are gently warmed up to about 60–70° C. by admitting steam to the jacket. At this temperature the action becomes exothermic and proceeds spontaneously of its own accord, reaching a temperature of about 100°C.

This is allowed to reflux for about half an hour. Distillation is then commenced and matters are so arranged that about 1 gallon of water comes over every 3 to 3½ minutes, adjustments being made in the heating and cooling arrangements if necessary.

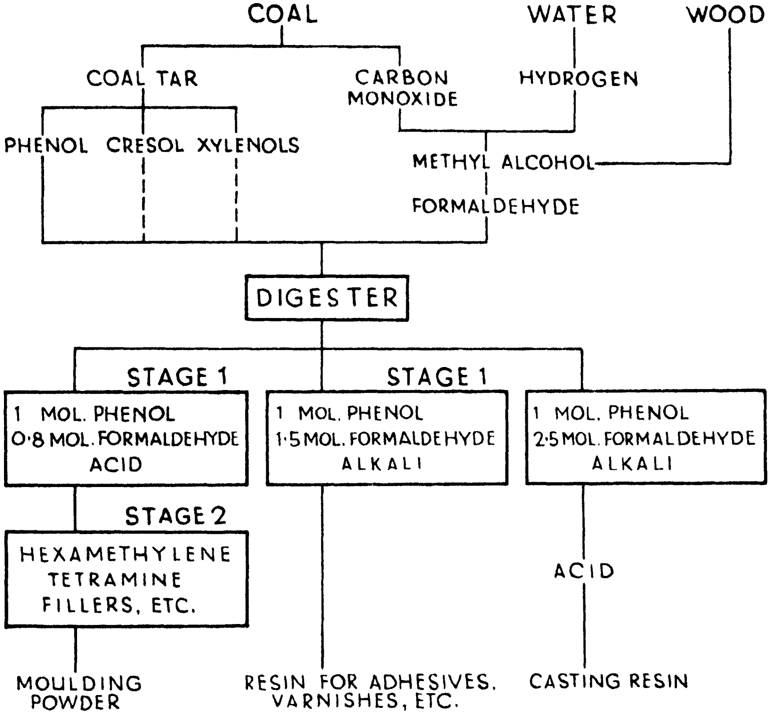


Fig. 30. Phenol-formaldehyde resins

As soon as 40 gallons of water have come over, the stirrer is stopped for a moment, the vacuum pump is switched into operation and the tap at the top of the pan admitting air opened a little, in order to inhibit excessive frothing.

The stirrer is then started and the remainder of the water removed under vacuum. It is usually necessary to turn steam on to the jacket shortly after the application of the vacuum in order to counteract the temperature drop.

Phenol-formaldehyde resins are available in two forms. The first is a syrup employed for cements, impregnation and the like, and the second a solid used for moulding powders and the making of lacquers.

According to whether a liquid or solid resin is required, so the cooking of the resin in the digester is stopped at an earlier or later stage. The transformation from a thin liquid resin to a thicker one, and so to a solid, with progressive increase in viscosity and melting point, proceeds evenly as heat is applied. When the operation is performed without stirring, the initial liquid resin can be observed to settle out to the bottom as a clear yellow mass with an aqueous layer on top.

Samples are withdrawn from the batch from time to time and tested for "feel," and, if a liquid resin is to be produced, for viscosity.

Melting Point and "Feel" of a Solid Resin. When a solid resin is produced it is tested for melting point and "feel." It should be bright and clear and should crumble readily in the fingers without being sticky. If it is tacky, the dehydration is incomplete. When the resin is ready it must be emptied from the pan and cooled as rapidly as possible.

Cooling is carried out by running the resin out in long, shallow trays, measuring anything from 5 to 12 feet long and 2 to 4 feet wide and a few inches deep. Several trays may be used for one batch, and the last traces of resin can be blown from the still by reversing the vacuum pump and using it as a compressor.

Impregnating Varnish. Sometimes it is desired to make an impregnating varnish for armature coils and the like, in which case, water is circulated vigorously in the jacket to cool the contents of the digester somewhat, and rather more than an equal weight of industrial spirit is added slowly with stirring. The varnish is always tested for solid content and viscosity. A varnish such as this, suitably dyed, may be used for staining electric light bulbs. It is also used for making moulding powders by the wet method, i.e. mixed with wood flour or asbestos and then dried in a vacuum oven. The yield of resin obtained from a batch such as that indicated is usually of the order of 55–60 per cent, or slightly more if a liquid resin is being prepared.

A Two-Stage Anhydrous Resin. Anhydrous resins are prepared for special purposes. A typical two-stage anhydrous resin can be made as follows: Cresol and 2 per cent of hexamine crystals are fed into the heated digester. When the temperature reaches 140°C. a vigorous reaction commences and the steam is turned off as the pressure may rise to 80 lb. per sq. in. inside the pan on account of the ammonia evolved. The steam is turned on again when the evolution of ammonia ceases and heating is continued for 3–5 hours at 165°C. to eliminate traces of the gas. Cresol is volatile in steam and if necessary, free cresol may be removed by blowing steam through the mass. The fusible resin is then allowed to cool to 100° C. and a further 10–12 per cent of hexamethylenetetramine added The ammonia which is evolved can be bubbled into formalin, so to produce more hexamethylenetetramine.

Large-scale Procedure for making a Two-Stage Phenol Resin and Moulding Powder. A typical American procedure used for making a two-stage resin on the largest scale has recently been described.[12] The process is carried out in a giant steam-jacketed steel kettle having a capacity ranging from between 1 to 15 tons of finished resin. Solutions of phenol and formaldehyde from enormous storage tanks are transferred into the steel kettle being weighed by photo-electric controlled machines. In order to keep it fluid the phenol is maintained at ·45°C.

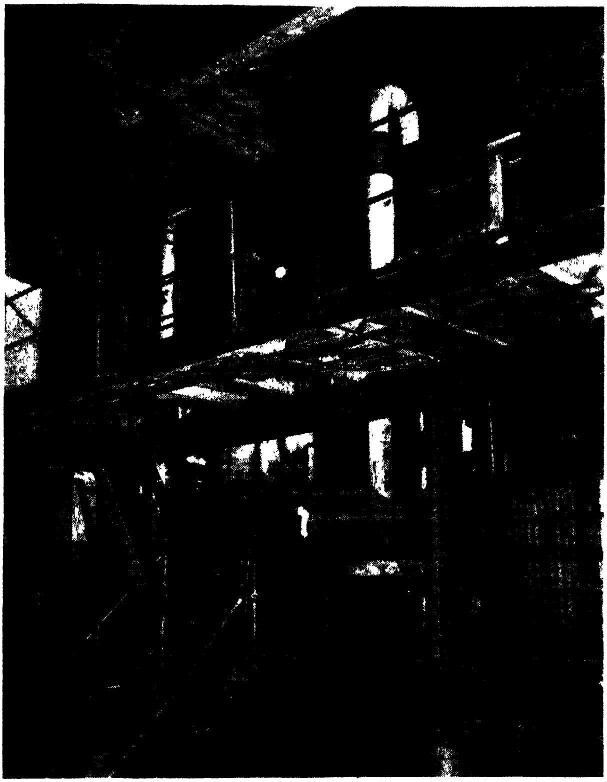


Fig. 31. Some of the reaction vessels for making phenol-formaldehyde resins[25]

A trace of sulphuric acid is added to catalyse the reaction. Steam up to 150 lb. sq. pressure is passed through the jacket. A very high vacuum is also applied. The kettle is fitted with a slow speed agitator. The actual temperature employed may range from 80° C. up to 150° C. All temperatures and pressures are automatically controlled. The treatment is carried out for some hours until the mass has reached a heavy syrupy consistency. A large valve in the bottom is then opened, and the hot resin pours on to a steel floor forming a layer of between 2 in. to 4 in. deep. It is cooled for some hours and is then broken up. There is no tendency for sticking to the floor.

Fig. 32. Drawing off liquid phenolic resin from a still[25]

The resin is automatically weighed and then crushed in a rotary type of crusher to particles of $\frac{1}{4}$ in. to $\frac{1}{2}$ in. This then passes on to a roller mill which reduces the resin to a powder of 200 mesh. This is transferred for further processing by means of compressed air. It is passed to a mixer where such ingredients as a lubricant and any other material may be added. For example, with a two-stage resin the hardening agent such as hexamethylenetetramine can be added at this stage.

The resin is now processed to form the moulding material. Colouring matter, fillers, etc., are added in a big mixer of the Banbury type before rolling. About 90 per cent of moulding powders contain wood flour, which may be present in proportions up to 50 per cent of the total moulding composition. In the case of coloured products the material is mixed on a ball mill. With black or brown materials Banbury mixing is employed. The mixed powder is then passed to roller mills such as are used for rubber. The rolls are held at differential temperatures of 105°C. and 150°C. in order to prevent sticking. The rolling process makes the product homogeneous, and also advances the cure. The length of time of rolling varies with different types of material, and is controlled by the flow characteristics and other desirable factors. The material is then stripped and passed on to another set of rolls which further improve the homogeneity, and also further advances the cure. It is then ground to granular particles in a saw-tooth crusher. The materials are finally blended and packed.

German Methods. German production is typified by the following procedures which were in use at Troisdorf.[27]

The raw materials used were as follows:

Pure phenol—synthetic from Leverkusen, where it is made from benzene sulphonic acid.

Crude phenol—

45–55 per cent phenol
30 per cent cresols (about one-third m-cresol)
12 per cent xylenols
0·05 per cent pyridine
1 per cent unsaponifiable

Cresols are supplied to D.A.B. (German Pharmacopoeia) specifications.

Grade	*Approximate Composition*
D.A.B. 4 M.1.	28–30 per cent m-cresol, about the same p- the rest o- and xylenols
D.A.B. 4 M.2.	30–35 per cent ditto
D.A.B. 4 B.1.	38–42 per cent ditto.
D.A.B. 4 B.2.	42–45 per cent ditto
D.A.B. 4 B.6.	50 per cent m-cresol, 50 per cent p-cresol

Phenol mixture S.R.I. is a mixture of phenols obtained from Leuna. This is used for making resins for moulding materials. Such moulding materials are slower curing at normal moulding temperature (150°C.) than standard grades, but if the moulding temperature is raised to 170°C. the rate of cure is not much slower than that of a standard moulding material at 150° C. Pure phenol moulding materials cure in 40–45 seconds. S.R.I. materials require 60–70 seconds.

Xylenols have a boiling range 210°–225° C.

High boiling tar acids, boiling range 225°–250° C., are used for making resins for laminated materials.

Storage—The phenol is stored as a 90/10 water mixture and consequently remains liquid at normal temperatures. Tanks are galvanised iron.

Formaldehyde is stored in the open in lagged aluminium tanks and the pipe-lines are aluminium or Mipolam.

Novolaks are made either by a semi-continuous process in which the condensation is done in one still and the evaporation in another, or by a batch process in a universal still suitable for either novolak or resole production.

The condensation still is fitted with a reflux condenser, but has no mechanical stirrer. Stirring is done at the start of the production by a stream of compressed air. The quantities of materials used are:

650 kg. phenol
65 kg. water
585 kg. formaldehyde
3·25 kg. oxalic acid crystals
0·5 kg. 100 per cent HCl as aqueous solution

The oxalic acid is dissolved in hot formalin. The phenol, which already contains the water given in the formula, and the formalin are measured. The contents of the still are thoroughly mixed by an air-stream and heated to the boiling-point as rapidly as possible. The mixture is kept refluxing for 60 minutes and 0·5 kg. hydrochloric acid (calculated as 100 per cent; used as 15 per cent) is added slowly. The addition of hydrochloric acid requires 10 minutes and the charge is refluxed for a further 25 minutes. The reason given for the use of both oxalic and hydrochloric acids was that if only hydrochloric acid were used it would be impossible to control the reaction. The reaction mixture is then cooled to 75° C. by the addition of 200 litres of water. The mixture is allowed to settle for 30 minutes and the resinous layer is then forced by compressed air into the evaporator. The control on this part of the process is visual, the operator watching for water in the evaporator.

The evaporator is fitted with a stirrer, but has no condenser. In place of a condenser there is a copper tube open to atmosphere. Near the bottom of the tube there is an air injector. The evaporator is run with the manhole cover off and the air injector causes a through draught which removes water, formaldehyde, and free phenol. These are discharged to atmosphere. Evaporation is continued for 2 to 3 hours until the resin temperature reaches 115° C. The resin may be heated for a further 5–10 minutes under vacuum if required. The resin is discharged through a heated plug valve into trays, where it is cooled. The yield of novolak (containing about 3 per cent water) is 110 per cent calculated on the phenol.

There is no control other than accuracy of measuring on the charge to the still, and only time controls on the condensation. The final resin is controlled by viscosity, which is done in alcoholic solution in a Höppler viscometer. This viscometer is of the falling sphere type, the sphere being made of nickel or glass. The instrument is water-jacketed and can be tilted as required. For novolaks a solution of 50 gm. resin in 50 gm. alcohol is used.

Other novolaks are made in which the acid is neutralised by NaOH when the temperature reaches 100° C. during evaporation. The stated reason for this was to prevent staining of moulds during moulding.

Resoles—Resoles are made in a copper still, fitted with reflux condenser, distillation condenser, and stirrer. These stills are heated by hot water. Copper stills are preferred to iron, because the iron surface is rough and when the resin becomes thick, heat transfer is poor. This tends to promote local overheating. Copper stills have to be cleaned by round-headed hammers every ten batches. The process carried out in iron stills take one hour longer after the second batch and 2½ hours longer after the fourth. The charge is:

1,500 kg.	cresol
1,350 kg.	formalin
75 kg.	ammonia (25 per cent, specific gravity 0·90)

Yield 115 per cent calculated on cresol (water content 3 per cent).

The cresol is adjusted, if necessary, to have a m-cresol content of 38 per cent. The charge is brought to the boil in 45 minutes and is refluxed for 50 minutes. It may also be digested at 85° C. for 105 minutes. At the end of the condensation period a vacuum of 50–60 mm. Hg. is applied and the resin is evaporated. The initial temperature is 45° C., and it is raised to a final temperature of 75°–78° C. under a pressure of 30 mm. Hg. The heating is done by circulating water as 90°–100° C. in the jacket.

The period of distillation is controlled by viscosity, the first test being made when the resin becomes so stiff that the stirrer is stopped. The viscosity is done in acetone (50 gm. resin : 50 gm. acetone) by the Ostwald method.

When the desired viscosity has been reached the resin is discharged by air pressure through a heated plug valve around which is fixed a loosely woven fabric bag filter. The resin is collected in trays 38 by 76 by 7·5 cm. holding 25 kg. These are immediately plunged into a tank of cold water.

Tests on Ammonia-Free Resins in Moulding Materials.

Ammonia. The test for freedom from ammonia was done as follows: A test tube was filled to the extent of 6–8 mm. with moulded pieces and 10 drops distilled water were added. In the test tube was placed a glass tube with two layers of absorbent packing between which was a layer of red litmus paper; the whole was held in position by adhesive tape. The test tube with the moulded pieces was heated in boiling water for 20 minutes. At the end of this time there should be no change in the colour of the litmus.

Free phenol—Free phenol was also estimated at Troisdorf, though this estimation was not required by Government specification. Two methods were used:

(1) *On ground mouldings.*

The maximum amount of phenol permitted was 200 mgr. in 100 gm. of ground material.

The ground mouldings were covered with distilled water and maintained at 80° C. for 1 hour. Phenol was estimated as tribromo-phenol or colorimetrically by Millons Reagent.

(2) *On whole mouldings.*

Permitted limits, 1 : 10,000.

The moulding was covered with distilled water and extracted at 80° C. for 1 hour. 12 c.c. of the extract was mixed in a test tube with 2 drops concentrated HNO3 (58 per cent) and 5 drops Millons Reagent. The test tube was allowed to remain for 1 hour at 80° C. in a thermostat, was then cooled and the red colour was compared with a standard. The red colour must not be deeper than that given by a standard of 1 phenol in 10,000. The standard contained 0·1 gm. phenol in 1 litre of distilled water.

Chemistry of the Phenolic Resins. Apart from relatively few known facts about the behaviour of phenols and formaldehydes, the chemistry of the reaction is still obscure, confused, and controversial. This is largely due to the alternative procedures which are available to make the resins and the many other variable factors concerned. It is interesting to consider the facts.

It is known that phenols, cresols, xylenols, etc., form resins with formaldehyde.

It is found that resins which set readily to the infusible, insoluble condition, are only formed from those phenols where the ortho and para positions are open and free, for example, in phenol, meta-cresol, and 3 : 5-xylenol.

It is found that symmetrical 3 : 5-xylenol with its three reactive positions, reacts to form a setting resin more rapidly than meta-cresol, which is in turn faster than phenol.

TABLE 33

PHENOLS FROM TAR ACIDS ON PRODUCTION BASIS OF 65,000 TONS PER ANNUM

Product	Per cent	Potential Production Tons
Phenol	20	13,000
Ortho-cresol	13	8,500
Meta-cresol	16·5	10,500
Para-cresol	11	7,000
2·4 Dimethylphenol	6	4,000
2·5 Dimethylphenol	3	2,000
Para-ethylphenol	2	1,300
3·5 Dimethylphenol	4	2,500
3·4 Dimethylphenol	2	1,300

Apart from these, the other phenols also form resins. These, however, are generally permanently fusible. In a few cases they can be persuaded to set, but with great difficulty, and very slowly. This occurs, for example, in the case of ortho-cresol. These fusible resins have their fields of application, notably in the coating industries, by virtue of the fact that many of them are soluble in oils, and compatible with them. Since the rapidity of setting is an outstanding requirement for commercial resin, they are undesirable for moulding resins, and are not used. Commercial thermosetting resins are therefore almost exclusively based on phenol and meta-cresol.

Theoretical Implications. In explanation of the importance of the ortho and para positions it is thought that in resin formation the phenol groups join up together through formaldehyde linkages which in the first place are formed at the ortho position. In this way a linear macromolecule is formed. It is generally accepted that linear molecules are fusible and soluble. The formation of cross linkages between such linear molecules which results in the formation of a three-dimensional macromolecule, can then occur at the reactive para position, which is still vacant. When this takes place the resin becomes insoluble and infusible, i.e. it sets.

It is known that phenol first of all reacts with formaldehyde to yield saligenin. Apparently formaldehyde will only act with phenol in the ortho and para positions. The ortho position is the more reactive.

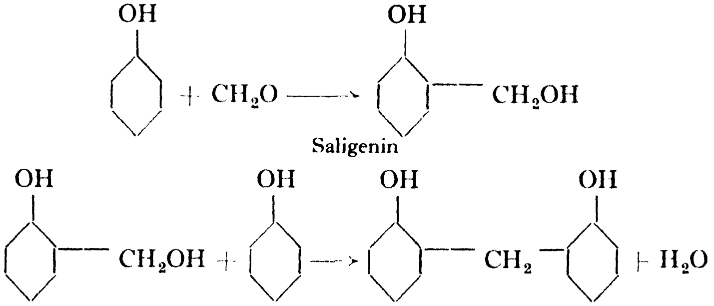
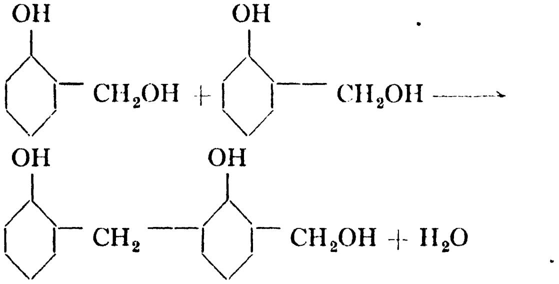


Fig. 33. Formation of Saligenin and Resol or A Resin

The next stage is



which with more saligenin goes to resitol.

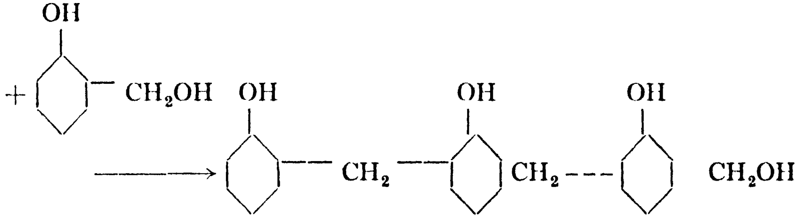


Fig. 34. Formation of Resitol or B Resin

Saligenin is the product formed in the ortho position. There is evidence that suggests that saligenin molecules thereafter combine with each other or with phenol to give high molecular weight products.

Saligenin forms chains soluble in acetone and alcohol. Open chain formula would account for this and the thermoplasticity. It goes to resitol under heat, thought to be due to the formation of straight chains where phenolic nucle are joined by methylene bridges. When further heat is applied a three-dimensional network is rapidly formed which would account for the infusible condition and the insoluble character of the final resin.

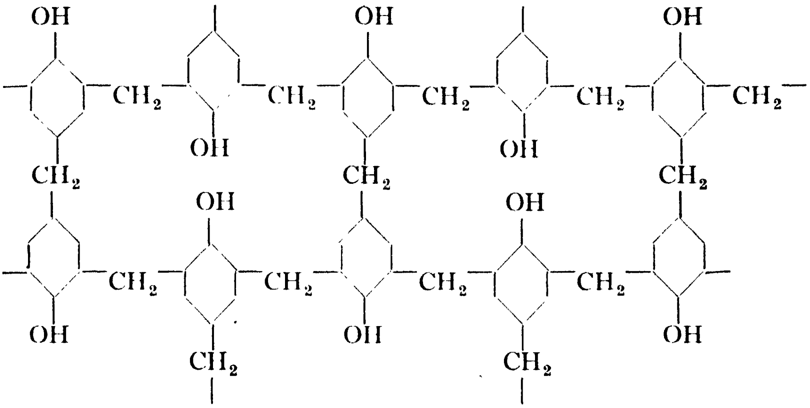


Fig. 35. Formation of Resit or C Resin

Further light is thrown on the composition of these materials by working with cresols where one active position is blocked. Para-cresol and ortho-cresol give condensation products which can be made infusible and insoluble only with great difficulty. This is attributed to the fact that the conditions will allow the formation of straight chain compounds or even branched chains which will provide a certain degree of steric hindrance with a corresponding degree of insolubility or infusibility. Yet the conditions are not such as lead to cross linking and the formation of a three-dimensional structure. Meta-cresol by contrast, gives such products quite readily.

Novolaks. The one-stage resin is usually easily heat-setting, while the two-stage resin is ordinarily novolak, which sets only with difficulty.

PER CENT OF ACID CATALYSTS USED IN NOVOLAK PRODUCTION[6]

(Based on the weight of the phenolic component)

Hydrochloric acid	0·15–0·3%
Sulphuric acid	0·15–0·3%
Oxalic acid	1·0 –1·5%
Phosphoric acid	1·0 –1·5%

Koebner[8] has shown that the molecular weights of novolaks reach about 1200 before they begin to become insoluble. He has shown that the molecular weight varies according to the amount of phenol and formaldehyde in the original mixture.

TABLE 34

KOEBNER'S EXPERIMENTS WORKING WITH 940 GM. OF PHENOL

In Exp. No.	Gm.mol. Formaldehyde	Yield of Resin	Viscosity	Mean mol. weight
1	1	180	25	229 Dioxydiphenylmethane
2	2	335	27	256
3	3	470	30	291
4	4	590	33	334
5	5	710	37	371 Novolaks
6	6	810	50	437
7	7	870	65	638
8	8	953	148	850
9	9	1,050	276	1,000
10	12	?	?	? Resit

For example, a product of average molecular weight, 638 was formed in a mixture containing 0·7 mol equivalents of formaldehyde. In contrast to this, the *resols*, when alkaline catalysts are used, begin to become insoluble with a molecular weight of only 300 or 400; i.e. there is a much shorter chain length.

In this connection Koebner has put forward a simple theory which has many attractions and explains many of the observed phenomena. He maintains strongly that there is no fundamental chemical difference between *resits* and novolaks.

He carried out an interesting series of experiments with varying proportions of formaldehyde, keeping other conditions constant. He employed concentrated hydrochloric acid as catalyst. With low proportion of formaldehyde crystalline mixtures of dihydroxy dimethyl methane were obtained.

Up to nine molecular equivalents of formaldehyde to ten equivalents of phenol yielded fusible resins which he regarded as novolaks, but with twelve molecular equivalents of formaldehyde the resin obtained is infusible and insoluble; in other words, a *resit*. The demarcation stage is fairly well defined. He carried out experiments on the physical characteristics of the resins obtained, found their viscosities and the mean molecular weights. Both these properties showed a steady increase in values as the proportion of formaldehyde present increased. In the case of nine molecular equivalents of formaldehyde the molecular weight was 1,000. In this instance Koebner suggested that there were chains present composed of at least ten phenol nuclei on the following lines:

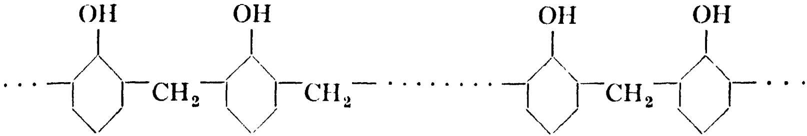


Fig. 36

The standard commercial novolak is based on one mol phenol and 0·8 mol formaldehyde, which gives a linear polymer similar to the above but with only seven phenolic nuclei.[3]

The final hardening of a novolak takes place by the same type of reaction as that which takes place in the formation of *resit.* The development of cross-linkage between molecules under the influence of heat causes the formation of three-dimensional molecules. One part of such a molecule might be:

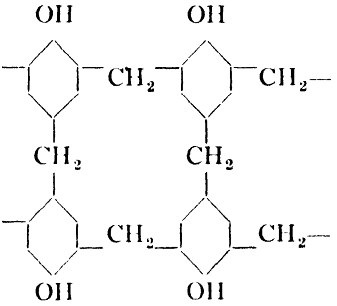
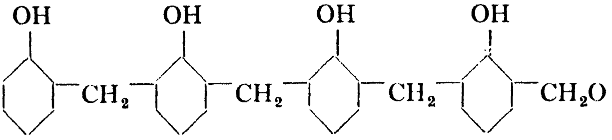


Fig. 37.

According to Koebner if the molecular weight of the novolak is 700 at the start, then the product of the first cross-linkage reaction is over 1,400, the next over 2,900. It can readily be seen that comparatively few reactions may result in a very large increase in average molecular weight, accompanied by a corresponding decrease in solubility and thermoplasticity.

In the case of the *resols* the total required amount of formaldehyde is present throughout the entire process. Polyalcohols are formed in the preliminary stages. These favour the occurrence of cross-linkages *at an earlier stage* than in the novolak process. Thus it is difficult to isolate soluble and fusible materials of molecular weight higher than three or four hundred. A typical *resol* would be:



Weith[24] has stressed one point of great importance, which apparently has not been fully appreciated. It has served as a useful basis for predicting the course of the reaction and the nature of the products formed under varying conditions. In the two type reactions represented by the equations:

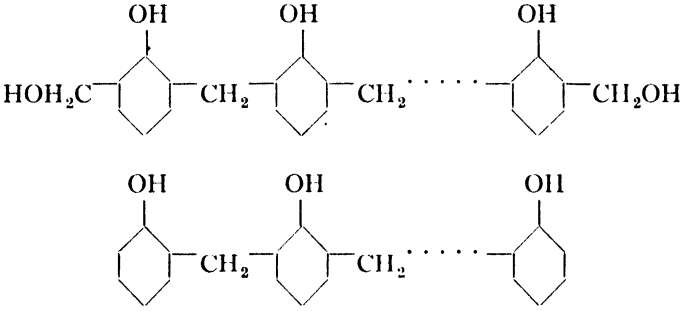


Fig. 38

alkaline catalysts promote the first reaction but are very noticeably less effective in causing the second reaction to take place.

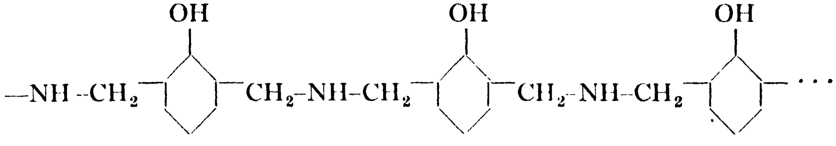
Acids on the other hand, have a very strong accelerating effect on the latter reaction. They probably speed the former also, although with an acid catalyst the rate of the first reaction is never appreciably faster than the second. The difference in the relative effectiveness of the two types of catalysts provides the key to an understanding of the apparently basic difference between the one-step and two-step processes. The two types of reaction illustrated above are essential to each process, but the real difference is in the relative speed with which the two types of reaction takes place.

In the one-step process, the formation of the poly-alcohols takes place *very rapidly*, while the further reaction of these alcohols with phenol or more oxybenzyl alcohol is *slow*. Thus a large amount of formaldehyde may be reacted in while the molecular weight remains comparatively low. Therefore a *resol* containing a larger number of reactive $-CH_2OH$ groups is formed.

In the two-step process the combination of phenol alcohol with phenol, or with compounds of the dihydroxy diphenyl methane type, or with more poly-alcohol, takes place very rapidly, while the formation of the poly-alcohol is less rapid. As a result the formation of the poly-alcohols is reduced to a minimum and the tendency is towards the formation of longer more linear moleculars.

A third factor which Weith has stressed is the effect of heat. The relative effect of heat on the two reactions is not known, but it certainly serves to speed up each type to a marked degree. In the hardening of a novolak with hexamethylenetetramine, the catalytic effect of the ammonia is probably chiefly to cause combination of the formaldehyde in a form analogous to the $-CH_2OH$ group, while the actual linkage of the molecules is brought about chiefly through the effect of the high temperature used in the final hardening process. Similarly, the hardening of a *resol* apparently is due less to the catalytic effect of alkali than to the effect of heat.

In connection with the action of ammonia as a catalyst, Redfarn[19] considered that the ammonia is bound in some manner as in the following scheme:



He considered that in one-stage resins the amino groups would probably be fairly evenly distributed between the chains, whereas in two-stage resins they would probably be mainly on the bridges.

The Action of Catalysts. The action of alkaline catalysts has been given close examination.

The quantities of ammonia recommended vary from 1 to 10 per cent of the total weight of the total reactants, and from 1 to 5 per cent in the case of aniline as a catalyst. Dry ammonia gas has been used at times, and at other times ammonia or ammonium carbonate has been employed as condensing agent for a preliminary condensation, followed by further reaction with acid as the catalyst to complete the process at a higher temperature after viscosity has set in.

A number of materials are known which may retard the reaction. Thus toluidines, xylidines, benzidine, or diphenylamine are claimed to retard the hardening of resin derived from phenol and hexamine, in effect acting as a negative catalyst.

The order of activity is evidently a matter of some importance owing to the importance of the factors of time and cost of maintaining materials under specified conditions. Holmes and Megson[5] have studied this question not only in the case of ammonia and amines, but also included the inorganic alkalis for comparison. Meta-cresol was used in place of phenol, and the reaction was carried out in the presence of 0·75 gm. of each base with half this quantity in the case of a diamine with two reactive radicals. Tar fractions boiling at 180–190°C. were also condensed with formalin and the order of reactivity noted. The reaction times in minutes were:

TABLE 35

Ammonia	34	Diethylamine	53
n-Propylamine	101	Trimethylamine	36
Ethylene diamine	22	Caustic soda	27
Dibenzylamine	270	Ethylamine	49
Pyridine	250	Benzylamine	300½
Caustic potash	29	Dimethylamine	16
Methylamine	26	Di-n-propylamine	83½
Isopropylamine	100	Lithium hydroxide	24½
Hexamine	32		

TABLE 36

NORMALITY OF ACID REQUIRED TO GIVE A RESINIFICATION TIME OF 50 MINUTES[6]

Hydrochloric acid	0·0019 Normal
Nitric acid	0·0019 ,,
Sulphuric acid	0·0019 ,,
Trichloracetic acid	0·0031 ,,
Oxalic acid	0·0054 (?) ,,
Phosphoric	0·0054 ,,
Dichloracetic	0·015 ,,
Monochloracetic acid	0·097 ,,
Formic	0·29 ,,
Lactic	0·37 ,,
Acetic	0·24 ,,

Phenol-furfural Plastics. A very interesting group of moulding resins is obtained from phenol and furfural. These are much more specialised than the phenol-formaldehyde resins probably owing to the fact that furfural is prepared by comparatively few concerns. The preparation of the resins follows closely along the lines described for phenol-formaldehyde resins. The furfural merely takes the place of formaldehyde. Different condensing agents yield a variety of resins.

A dark brown resin, fusible and soluble, was prepared by Kurath[11] by using sodium hydroxide. One hundred and eighty-four parts furfural were added to 188 parts phenol and 10 parts 10 per cent sodium hydroxide, and the mixture heated so as to give a constant distillation rate when the maximum temperature in the reaction vessel was 184° C. To obtain a thermosetting material, the initial soluble resin was mixed with hexamethylenetetramine.

The resins obtained are invariably dark in colour, and consequently products based on these resins are nearly always brown or black.

Moulding powders are found to be rather slower setting than the phenol-formaldehyde powders, which is of course a disadvantage. They do not flow anything like so well as phenolic resins. They were the first resins to be used for transfer moulding. The mouldings have a number of attractive properties. Peters[14] has described some of the desirable properties. The mouldings show very little shrinkage and give excellent reproduction. They are able to withstand high temperatures, for example, a continuous temperature of 230° C. They have good resistance to tracking, and are, in fact, widely used for electrical parts which may become heated, e.g. distributor caps and other parts of ignition systems.

Their importance has been stressed for cold moulding applications, notably for making moulded abrasive wheels. They can be used for unconfined mouldings and have found application for printing plates, etc.

The resins have other applications as adhesives, impregnating agents, and so on.

REFERENCES

1 AYLSWORTH. U.S.P. 1,020,593, *J.S.C.I.* 1912, **31**, 399.
2 BAEKELAND. *Ind. Eng. Chem.*, 1908, 1, 149; B.P. 1921/1908.
3 BAEKELAND AND BENDER. *Ind. Eng. Chem.*, 1935, **27**, 225.
4 BAEYER. *Berichte*, 1872, **5**, 1094.
5 HOLMES AND MEGSON. *J.S.C.I.*, 1933, 415T.
6 JONES. *Plastics Monograph*, No. 11, p. 59.
7 KLEEBERG. Ann. 1891, **263**, 283.
8 KOEBNER. *British Plastics*, 1942, **14**, 100.
9 LEBACH. *Z. angew. Chem.*, 1909, **22**, 1599.
10 LUFT. B.P. 10,218/1902.
11 KURATH. U.S.P. 1,969,890/1934.
12 Monsanto Chemical Corp. Technical Literature.
13 OTHMER AND LEYES. *Ind. Eng. Chem.*, 1941, **33**, 158.
14 PETERS. *Ind. Eng. Chem.*, 1936, **28**, 755.
15 Petroleum for formaldehyde. *Chem. Met. Eng.*, 1942, **49**, 154.
16 PRAHL AND MATHES. U.S.P. 1,964,768/1934; 2,035,917/1936.
17 RASCHIG. *Z. angew. Chem.*, 1912, **25**, 1945.
18 Raschig Process. Durez Corp., see *British Plastics*, 1940, **12**, 139.
19 REDFARN. *British Plastics*, 1942, **14**, 9.
20 SMITH. *J.S.C.I.*, 1899, **18**, 1029.
21 STORY. *J.S.C.I.*, 1906, **25**, 195; B.P. 8,875/1905.
22 United States Phenol Production. U.S. Tariff Commission.
23 WAKEMAN AND WEIL. *Ind. Eng. Chem.*, 1942, **34**, 1387.
24 WEITH, "*Polymerisation*," Reinhold Publications Inc., New York, p. 207.
25 Illustrations by courtesy of Bakelite Ltd.
26 " " I.C.I. Ltd.
27 C.I.O.S. XXXIII-23, p. 39.

CHAPTER V

APPLICATIONS BASED ON STRAIGHT PHENOL-FORMALDEHYDE RESINS

WHILE the largest quantities of phenolic resins are employed for making moulding powders, yet considerable amounts are used for a variety of applications without further processing. Such uses as varnishes, cements, impregnating media, lamination, involve the preparation of solutions by the straightforward addition of alcohol or acetone to the resins. Modification of the resins, e.g. production of oil-soluble types, etc., is left for a later stage in the discussion.

Heat-hardenable Varnish. Phenolic resins are used for varnishes, enamels, lacquers and cements of the heat-reactive type, i.e. which may be set by heating. One-stage resins are usually employed, in which the reaction has only been carried part of the way, so that a solid resin has not yet formed. This syrup is normally taken up with industrial spirit although other solvents may be used. Solid resins in the *resol* or A condition may be used. In their primary state resins, which are employed to produce these products, will dissolve in common solvents, such as alcohol and acetone. Application of heat causes them to harden and solidify after which they are permanently insoluble and infusible. The industrial importance of these products may be attributed to this chemical change.

These solutions of phenolic resins are general-purpose materials used for impregnation, adhesion, and coating. Natural gum varnishes attain their final protective properties by drying and oxidation in the air. By contrast, phenolic resin varnishes attain their best properties by being baked at elevated temperatures after they have been applied. The protective properties of the coatings are far superior in many respects to varnishes made with natural gums.

After the phenolic varnish has been applied the article is baked first to expel the solvent and then to convert the synthetic resin coating to its final infusible, resistant and durable state.

Properties. Phenolic varnish provides a hard, continuous uniform coating for metal. When applied to wood or porous ceramic material it can serve as impregnation or surface coating, depending upon the properties desired in the finished work. The resin film is a good electric insulator. From a mechanical standpoint, it provides a tenacious and durable bond. It is non-hygroscopic, and is unaffected by extremes of climate—temperature or humidity. It does not deteriorate, and is unaffected by water, alcohol, acetone, benzene, and other common solvents, oils, greases, organic acids, dilute mineral acids, and most of the soap lubricants. Once converted to the final durable state it does not melt at any temperature, and will not char at temperatures below 150°C. The heat resistance is higher than that of any other type of organic varnishes. Special phenolic varnishes have been developed which will withstand even higher temperatures.

Phenolic resin varnish is extensively used in the electrical industry as an insulating bond for coils, armatures and windings. It is used for such purposes because of its high mechanical bonding strength, dielectric value, and resistance to oil, grease, water, dirt, and petrol.

Applied to paper or cloth-winding strips, it provides a convenient taping material for the insulation of bus bars, and conduits.

Phenolic resin varnish is also used in the manufacture and repair of motor and generator armatures. By virtue of the excellent ranges of properties it serves to increase the durability of armatures. Armatures so treated have good temperature resistance, and do not burn out under temporary over-load. The varnish impregnation imparts high mechanical strength to the fabricated unit.

Phenolic varnish is also used as an armature impregnation for small power tools and for heavy electrical industrial equipment.

Protective Coatings. Phenolic varnish has many applications as a protective coating for metal, wood, ceramic materials, and many other substances. A few outstanding fields of application which very effectively illustrate this properly include:

(*a*) On chemical processing equipment exposed to corrosive atmosphere.
(*b*) On gas meters to resist attack of hydrogen sulphide.
(*c*) On interiors of tank cars.
(*d*) On industrial equipment to resist weak acids and alkalis; corrosive fumes, alcohol, petrol, and many other solvents.

Special baking varnishes have been developed for the protection of parts and equipment employed in textile manufacture. These coatings are especially valuable for aluminium spools exposed to alkaline solutions, iron and steel parts, exposed to acid conditions, dryers, etc., and in general wherever resistance to chemicals is required. Paper wound tubes for textile yarns when impregnated with phenolic varnish are found to withstand the action of water, dyes, and bleaches.

General Utility. By far the largest field for heat-hardenable varnishes is for impregnating sheets of paper or fabric to produce laminated materials (*v.i.*). These impregnated sheets are superimposed up to desired thicknesses and then subjected to heat and pressure to form a solid, homogeneous stock. The material is commercially available in sheets, tubes and rods and special forms.

Phenolic varnish is extensively employed for numerous industrial applications. To indicate its versatility, a few examples may be cited as follows:

(*a*) Impregnation of coil windings.
(*b*) Bonding agents for abrasive wheels.
(*c*) To impregnate asbestos commutator rings.
(*d*) To impregnate asbestos composition clutch rings used in car manufacture.
(*e*) As an impregnation material for corks, friction blocks, or pulleys.
(*f*) As surface coating for plaster of Paris castings.
(*g*) As a binder for core sand in the foundry field. When mixed with sand and other fillers it may be used to patch large cores.
(*h*) To impregnate motor-brake linings.
(*i*) As a bonding agent for wood veneers and plywoods.
(*j*) To cover woven wire screen filters.
(*k*) To coat metal developing racks to resist the corrosive effect of photographic solutions.

Methods of Application. Phenolic varnish is applied by spraying, brushing, or dipping. Selection of method will depend on several factors such as size of piece to be treated, scale of operation, design of piece, and thickness of coating or extent of impregnation desired.

Dipping Process. The treatment of small items may be carried out on a large scale by means of a dipping process. Continuous production units are designed so that the parts are conveyed through a tank containing the phenolic varnish, then through a dryer to dispel solvents, and finally to an oven where the ultimate baking is achieved. Hand-dipping is widely practised, while there are many simple mechanical devices to raise and lower objects of large weight into the dipping tank.

Surfaces to which varnish is to be applied should be dry, and free from grease, rust, or scale. Sand-blasting or washing with grease remover is recommended.

When more than one coat is necessary, then after applying each successive coat, the work should be baked just sufficiently to dispel the solvents. For small work, the initial baking may require about 15 minutes at a temperature of 80°C. The final coat should be given a longer baking at higher temperatures. Conditions for this final baking will depend upon the size and nature of the work. Satisfactory results are not usually obtained below 110°C. Small articles require baking for three hours at 120°C., or 150°C. for one hour.

Coil Impregnation. The impregnation of electrical coils is a major field of application. Three methods are widely used for coil impregnation, namely, dipping, double dipping, and vacuum impregnation. Coil impregnation practice differs somewhat from the methods used to coat non-electrical equipment. In coil impregnation the main purpose is to secure an insulating effect by penetration of the varnish. The varnish usually contributes to the mechanical strength of the finished unit, in addition to improving the insulating and corrosion-resisting properties.

When winding coils for phenolic impregnation, it is essential to omit insulating materials containing oils, paraffins, or other non-absorbent substances. To secure best results, the coil should be wound with untreated tape or paper.

After impregnation, and prior to the baking operation, coils retain their flexibility for some time, so that wire can be bent and otherwise manipulated without injury to the insulation.

Special types of phenolic varnish have been developed to impregnate enamelled wire coils and armatures. This varnish will not attack enamelled wire which has been properly baked. It possesses good electrical properties, good bonding strength, heat resistance and solvent resistance.

A Typical Dipping Process for Coil Impregnation. The dipping process of coil impregnation involves the following steps:

1. Moisture is driven from the coils by baking at 105°C. for at least 3 hours or longer, depending upon the size of the coils.
2. While the coils are still hot, they are immersed in varnish, for 15 to 30 minutes, or until bubbling ceases, at which time they should be removed. The specific gravity of the varnish solution employed in this operation is determined by the particular type of phenolic varnish used and the nature of the work.
3. Coils are withdrawn slowly so as to ensure a smooth, uniform coat. They are drained for one hour, and baked in an oven at a temperature of 75°C. The time of baking will normally be about 6 hours.
4. The temperature is raised to 120°C. and baked from 12 to 24 hours. Time of baking will be governed by the size and construction of coils.

Reclaiming Porous Castings. An excellent illustration of the service which plastics materials can render to industries with which they are often thought to compete, is the use of phenolic resins for reclaiming porous castings. The new technique is a profound contribution to the metal industries.

Metal castings are often porous, although the defect is frequently quite slight. Nevertheless, the porosity may be sufficient to cause rejection of the casting. Phenolic resins provide an efficient and simple remedy. Two types of solutions are employed: (*a*) a clear solution for cases where only fine pores exist, and (*b*) a solution containing mineral filler when the porosity is more marked. Such solutions may be used for ferrous and non-ferrous metals, and have proved highly effective.

Two methods of application are employed[11]: for a small casting, the resin solution is forced into the casting by external pressure. For large hollow castings the resin solution inside is subjected to pressure so that it is forced through the walls from the interior.

Small castings can be treated by vacuum pressure methods. In this case the castings are placed in a strong container from which air can be evacuated. A suitable vacuum is developed and the sealing solution allowed to enter from a storage vessel until the castings are covered. Pressure is maintained for a suitable time, so that the resin is squeezed into the walls of the casting, thus filling the pores. The castings are removed from the vacuum pressure chamber, wiped and baked.

In the case of large hollow castings, one with several outlets may be considered. All the outlets except one are closed. The casting is filled with the phenolic solution through the remaining hole, and pressure may be applied there. It is found that air pressure from 50 to 150 lb. per sq. inch is adequate and forces the solution into the pores of the metal. The process is carried through until sweating is evident on the outside surface of the casting.

Another feature is the fact that the casting may be either in the raw state or machined. In any event, machining can subsequently be carried out. These processes are carried out at ordinary temperature. Some of the resin solution remains in the walls of the casting filling up any pores. This resin is set by baking. The phenolic resin is thereby converted from the soluble fusible state into the insoluble infusible material. Moreover, it is highly resistant to nearly every form of attack. The first stage of the baking removes any solvent, while further heating leaves the pores of the casting filled with the chemically inert resin.

The procedure may be summarised as follows:

1. After pressure has been exerted for some time, the casting is

drained and lightly wiped with alcohol. It is essential to remove the adhering material, because it may be difficult to remove after baking.

2. The casting is placed in a suitable oven, and is slowly brought up to a temperature of 85° C., taking about an hour.

3. When the solvent has been removed in this way, the temperature is taken to 110° C. for an hour, and finally given another hour at 135° C.

This method of salvaging castings has proved of profound value under war conditions. Innumerable porous castings have been put into service instead of being scrapped.

Heat-hardening and Self-hardening Cements Based on Phenol-Formaldehyde. Phenolic cements are closely related to phenolic varnishes, but are much more viscous. In addition to the resin and solvents a solid reinforcing filler is usually present. A general utility cement or plastic composition can easily be prepared by mixing finely ground asbestos into a solution of resin.

Another useful cement can be made by mixing red lead into a solution of phenolic resin. This material will withstand conditions of high pressure, steam, oil, etc. It tends to harden very rapidly, and should be prepared shortly before use.

Phenolic cements are available as (*a*) granular powders, (*b*) viscous liquids. The first type is made ready for use by the addition of solvents. The second may, if desired, be diluted with a thinner such as industrial spirit.

Cements for General Application. Phenolic resin cements are applied to a wide variety of organic and inorganic materials, such as wood, paper, fibre, rubber, porcelain, glass, concrete, metal, etc. They provide a strong and durable bond when fully baked. It is essential to bake in order to bring out the best properties of strength and resistance. After this treatment the product has become hard, non-hygroscopic, electrical insulating, and resistant to ordinary chemical reagents, such as alcohol, acetone, petrol, and dilute acids. Once the cement has been fully set, it no longer melts at any temperature, although it will char above 190° C.

These cements are widely used in the electrical industry for the manufacture of numerous articles, including commutators, transformers, and so on. They also feature in the preparation of scientific instruments for bonding metal, glass, porcelain, etc.

Surfaces to be cemented have to be thoroughly clean, so that sand-blasting is generally used to remove grease, rust, or scale. The cement is then applied. The parts are joined and after pressing firmly together are clamped into position. Small articles are heated at 80° C. for a time—between 1 and 4 hours. They are then baked for 2 hours at

120° C. Where a large amount of cement is employed the temperature should be lower, and the time of baking extended. The temperature of 80° C. should not be exceeded and the cement is hardened in some hours, finally being baked at a higher temperature. The use of higher temperature during preliminary baking may lead to porosity which weakens the joint. The heating is carried out in ordinary gas or steam ovens at atmospheric pressure.

The Applications of Phenol-Formaldehyde Resin Cements for Electric Lamp Bases. The strong mechanical bond obtained with phenolic resins is unaffected by temperatures developed in electric lamps. As a result these cements virtually monopolise the field for attaching electric-light bulbs to their bases. They are also employed in the production of valves of every description. The resin employed for fixing lamps is usually in dry powder form which contains all the necessary ingredients. They may contain filling materials. For example, one such cement contained:

Phenolic resin . . .	30 per cent
Silica	70 per cent

It is made into paste by mixing thoroughly one ounce of industrial alcohol to a pound of cement. Inadequate mixing impairs the adhesive properties, and any efficient paste-mixing machine may be employed. The paste is allowed to stand overnight before being applied.

Lamp-bases are filled in a standard base-filling machine, so that the paste forms a uniform narrow cylindrical ribbon inside the base, and near its upper edge. The filled bases stand for a time, so that some of the solvent evaporates.

Thereafter normal practice employs circular rotating machines heated by gas burners. The burners are adjusted so that when the finished lamp is in the machine the cement is set to the final infusible state.

Phenolic Cements for Brushes. Another outstanding industrial application of phenolic resins as a cement is in the manufacture of brushes. A phenolic resin is admirably suited for setting bristles in brushes. It is superior to other bonding materials such as rubber, because it is unaffected by benzene, oils, water, paint thinners, etc. As a consequence, phenolic cements are used in the manufacture of every type of brush, ranging from the smallest paint-brush to large power-driven rotary scrubbing brushes.

The cement is thinned to the proper consistency for penetrating the different types of bristle assemblies. These are arranged in the ferrule, and the cement is poured in at the top. It is allowed to stand until the cement has penetrated to the bottom of the ferrule. The resin cement must be completely set by baking because the bristle setting has to resist alcohol, benzene, oil, turpentine, water, etc. The brushes are then placed in racks with ferrule end downwards. The racks are brought on to a hot plate at 80°C. for about an hour. Thereafter the brushes are baked in an oven for 2 hours at 140°C. It is necessary to determine the right viscosity of cement and the best temperatures by experiment on the particular type of brush being made. These important factors will depend upon the nature and size of bristles and the type of ferrules being used. If the temperatures have to be lowered, then evidently the time of baking must be increased.

Synthetic Resin Adhesives. Glues and cements based on synthetic resins have profoundly influenced the whole field of adhesion.

In recent years adhesives based on phenolic resins in particular have acquired a new significance. This chiefly applies to the wood industries and associated activities. The resins have greatly aided production of plywood. They have expanded output and improved products. They have facilitated commercial production of curved shaped wood in an ever-growing range of contours. Completely new horizons have appeared. Synthetic resin adhesives have become a major industry.

They have been the cause of an entirely new perspective on the theory and practice of adhesion. Early ideas attributed the action of cements to the purely mechanical action of interlocking between the glue and the surface to be joined. De Bruyne[8] in particular has carried the subject forward so far as synthetic adhesives are concerned. It is now recognised that mechanical action does make a minor contribution to the strength of the joint. But the main action is due to physical-mechanical cohesive forces between the cement and the joint surfaces. Realisation of this principle has enabled the evolution of very satisfactory adhesives giving bond strength which was previously unattainable. Synthetic resins in particular play a leading part.

Traditional glues were based on animal or vegetable products, such as casein, bone glue, fish glue, starches, blood, etc. While effective in many respects, they all have outstanding disadvantages of one sort or another. In particular they are all sensitive to climatic changes. Moisture tends to ruin the adhesion. These materials are also subject to decomposition by fungi and bacteria which likewise destroy the joints.

In many fields of application plastic cements are displacing the older materials. The number of materials available grows rapidly. Their advantages may be summarised as:

(*a*) Resistance to water.
(*b*) High joint strength.
(*c*) Rapid setting which gives high production.

(*d*) Resistance to bacteria, fungi, insects, etc.
(*e*) Close control.

Phenolic cements based on phenol-formaldehyde resin are widely used in the manufacture of plywood and improved wood. This is an activity which is expanding at a most extraordinary rate. The cements give bonds which are stronger than the wood itself and, moreover, which are completely resistant to moisture. In many cases they will withstand the prolonged action of boiling water.

Phenolic cements are available either as liquid glues or as dry so-called glue films. These are tissue paper impregnated with phenol-formaldehyde resin (*v.i.*). The liquid glues generally take the form of an alcoholic solution of the phenol-formaldehyde resin. In many ways they resemble the impregnating solutions used for making laminated paper, fabric, etc. Such solutions may be applied without difficulty either by brush or by roller, or by dipping. Since the setting action implies the use of heat, these solutions are quite stable at ordinary temperatures, and can be kept almost indefinitely.

The phenolic adhesive may be applied to the wood surfaces, and these may be dried and allowed to stand for weeks before carrying through the actual pressing procedure. The phenolic resin adhesives are available commercially in three forms:

(*a*) for hot setting conditions without any further addition,
(*b*) for hot setting conditions with the addition of a hardener,
(*c*) for cold setting conditions with the addition of a hardener.

A number of concerns market such materials. In most cases the principle employed is the same.

There are two separate ingredients:

(*a*) The resin solution.
(*b*) The *hardener* (also referred to as the *accelerator*, *setting agent*, or *catalyst*).

The resin solution is useless without the hardener. However, once the hardener has been mixed into the resin then the useful life of the material is limited. This means to say that the setting action has begun, the mixture begins to thicken up, and after a time, which depends on the temperature, it can no longer be applied, and is therefore no longer useful for its designed purpose.

A typical procedure involves the addition of 10 parts of hardener to 90 parts of resin solution. These are vigorously mixed together so that there is thorough admixture. When this has been done it is found that the useful life of the mixture is 2 hours at 60° C., 1 hour at 70° C., ½ hour at 80° C.

As a rule such adhesives can be applied by brush to the surfaces being treated, requiring something of the order of 3½ to 4 lb. per 100 sq. ft. They can be thinned with industrial spirit.

In actual practice wood that has been coated with adhesive is not used immediately; it is allowed to stand for at least half an hour before being pressed. It may be allowed to stand at room temperature for hours without being affected. This is obviously a great advantage for it increases flexibility of production.

The conditions employed for preparing the plywood or, whatever is being made, generally involves a mechanical pressure of the order of 150 lb. per sq. in., and temperatures of 120° C. to 150° C.

The time required to make plywood will naturally vary with the thickness. A typical example, however, is the case of $\frac{3}{16}$-in. plywood which requires 8 minutes at 150° C., 10 minutes at 140° C., 15 minutes at 130° C., and 30 minutes at 120° C. These are extremely rapid by comparison with the lengthy periods required for cold-setting natural glues.

Cold-setting Phenolic Cements. Recently adhesives based on phenolic resins have been prepared which may be set in the cold without the application of heat. In this instance a resin syrup is prepared which is quite free from any solvent. It is absolutely essential in this instance to add a hardener to promote the setting action. In one such type[7] of cement the hardener is a strong acid and is added to the extent of between 13 and 16 per cent on the weight of the resin. The mixing is carried out with great care to ensure uniformity. Heat is generated during this procedure. Once mixed the material has a life at room temperature of about 2 hours, after which time it has become too thick to be applied.

The material can be applied by brushing, dipping, or roller spreading, and spreads at the rate of about 3½ lb. per 100 sq. ft. In this instance the surfaces are brought together almost immediately, and maintained under pressure while the adhesive is tacky. The period required for setting depends on the amount of setting agent. At 20° C., with the lower proportion of setting agent, the time is of the order of 4 hours; with the maximum amount of setting agent the time taken is 2 hours. At the end of these periods the pressure can be released, although the joins will actually continue to become stronger during something like 3 hours. These adhesives will set and give an effective join even if pressure is not applied. However, since the strength is dependent on a continuous film of resin, it is necessary to ensure that no gaps should be left.

P.600 Resin. The best-known German cold-setting synthetic glue is known as P.600 resin.[12] It was used for cold assembly work in aircraft construction. The composition was:

100 parts phenol
150 parts 30 per cent formalin
2·5 parts caustic soda (in 7·5 parts water)

These are refluxed for 12–15 minutes and then distilled for 5 hours at 20 mm.

12·5 parts paraformaldehyde
25 parts acetone

are added and refluxed for another 1½ hours. The material has a shelf life of 2 months.

A hardener is used, generally toluene- or benzene-sulphonic acid as a 50 per cent solution in water; 6 per cent is used on the phenolic resin. Pot life is about 4–5 hours at 20° C. Curing time is 12–15 hours for maximum strength (100–130 kg./mm.^{2}). The glue is not dependent on thin glue lines for strength; wide gaps, e.g. 5–6 mm. give normal strengths.

For cold-setting adhesives the following is used:

100 parts P.600
20 parts Hardener (50 per cent solution)

Modified Phenol-Formaldehyde Resins. One of the most important fields of application of phenol-formaldehyde resins is for coatings generally, as distinct from special types already described. The types of resins already described are not very suitable, and modifications of composition and technique are necessary. Oil-soluble resins have played a profound part in many improved types of coatings in recent years. Many combinations of phenol-formaldehyde resins and other synthetic resins are also employed. Oil solubility applies to the usual drying oils such as linseed oil, tung oil, treated castor oil, etc. Varnishes are ordinarily based on combinations of drying oils with natural gums and resins. Greatly enhanced effects have been produced by the incorporation of synthetic resins to replace the natural gums and resins.

There are three distinct procedures whereby phenol-formaldehyde resins may be rendered soluble in drying oils:

(*a*) Phenol-formaldehyde resins may be modified with rosin.
(*b*) The resins may be modified with drying oil.
(*c*) Completely oil-soluble phenolic resins may be prepared.

This type of material was first put forward by Berend[2] and Albert in 1912. They are similar in many respects to the materials known in this country as Albertols.[3]

Drying Oil Modified Phenolic Resins. Phenol-formaldehyde resins react more favourably with tung oil than with linseed oil, and tung oil is most widely used in making this type of product. The behaviour of tung oil and any products in which it features is largely conditioned by the heating treatment. In order to get a rapidly-drying product the tung oil must have been subjected to heating above 270° C.

Brown[5] heated 12 parts tung oil and 1·5 parts lead resinate up to 190° C. and held for 15 minutes. When cooked to 100° C., 4 parts cresol and 3 parts formalin were added. The mixture was heated at 100° C. for an hour, allowed to stand, and then heated at 150° C. until no free formaldehyde was present. It was thinned to give a baking varnish.

The general practice is to combine the drying oil with phenol before completing the reaction with formaldehyde. A typical procedure, according to Byck,[6] is to reflux the following composition for 6 hours:

100 parts phenol
150 parts tung oil
2 parts phosphoric acid

Thereafter, two successive portions of 10 parts hexamethylenetetramine were added. The material is then heated at 300° C. until it becomes extremely thick. It can then be dispersed in the usual varnish media to give a rapid drying varnish.

Another procedure[1] is to dissolve all the ingredients in a mutual solvent of high boiling point. The solution is then refluxed until homogeneous. The solvent is distilled off and further heat treatment is given until the resin acquires the desired consistency.

Oil-Soluble Phenolic Resins. Phenol-formaldehyde resins which are completely soluble in oils without any modifications have steadily gained importance in recent years. They are mainly based on substituted phenols. The number of phenols which may be used is very great owing to the success achieved by synthetic methods, but there are certain characteristics feature which are common to all of them.

Certain generalisations can be made concerning this development.

(1) *Ortho* substitution gives easily oil-soluble resins with acid or alkaline catalysts.

(2) *Para* substitution gives easily oil-soluble resins with acid catalysts. Alkali and high proportions of formaldehyde tends to give insoluble resins unless the reaction is stopped early enough.

(3) *Meta* substitution tends strongly to produce insoluble resins except in the case of symmetrical xylenol or when the substituent group is very large.
(4) Oxygenated substituent groups tend to produce insoluble resins.
(5) All *ortho* substituted phenols produce resins which yellow or darken on exposure to light.
(6) All *ortho* compounds produce resins which are slower in drying than the corresponding *para* compound.
(7) Alkaline catalysts generally give better drying materials than acid catalysts.
(8) *Para* substituted phenols produce resins which are superior in alkali resistance to the corresponding *ortho* or *meta* compounds. The phenyl group is especially powerful when in *para* position in promoting alkali resistance.

Up to the present time most of these phenols have not been available commercially, and expansion in such cases have waited in their availability. The most readily available materials have been the xylenols, obtained from coal-tar. These are in general more reactive towards formaldehyde than are phenol or the cresols. Of the isomers available the 1.2.4 xylenol appears the best for oil-soluble resins.

Oil solubility appears to depend largely on two factors: (1) the nature of the group which is attached to the phenol portion, and (2) the position of the substituents. The earlier consideration of the formation of resins has shown that meta-substituted phenols are the best for making thermosetting resins for moulding powders. For making oil-soluble resin it is found essential that the para group shall be blocked. Brittain[4] states: "Practically all of the substituted phenols which are used by the manufacturers at the present time are para-substituted phenols." The important positions for making oil-soluble phenol-formaldehyde resins are the ortho and meta positions which should be open." The ortho-substituted resins are not used at all in the manufacture of phenolic resins. According to Turkington and Allen[10] "the explanation lies in the fact that the three most reactive positions in the phenol ring structure are the para and the ortho positions. When any of these positions is occupied by a substituent group the tendency to form cross linked three-dimensional insoluble polymers with formaldehyde is diminished."

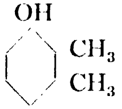
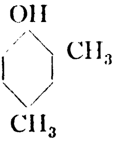
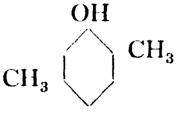
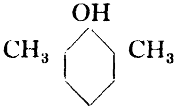
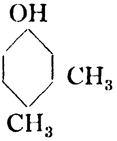
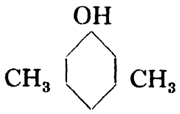
Usually, rather less than 1 molecular equivalent of formaldehyde is condensed with 1 molecular equivalent of the phenol.

In the case of these resins the type of catalyst markedly influences the resulting product. Alkaline catalysts form products which at first are oil-soluble, but which, on further heating, may become insoluble. This property is of considerable importance. It affords the opportunity of combining the outstanding properties of the phenolic resin with the drying behaviour of the oil. The following is a typical example:

75 parts p-tertiary butyl phenol
50 parts formalin
7·5 parts conc. ammonia

TABLE 37

XYLENOLS

Formula	Nomenclature	M.P.	B.P.
	1.2.3 Xylenol (o-3 xylenol)	73° C.	213° C.
	1.2.4 Xylenol (m-xylenol)	25° C.	211° C.
	1.2.5 Xylenol (p-xylenol)	75° C.	212° C.
	1.2.6 Xylenol (m-xylenol)	49° C.	202° C.
	1.3.4 Xylenol (o-4 xylenol)	65° C.	222° C.
	1.3.5 Xylenol (m-5-xylenol)	66° C.	221° C.

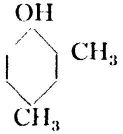
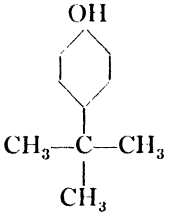
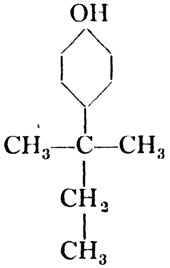
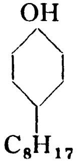
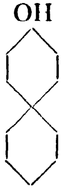
The 1.3.5 Xylenol is the most readily available and the cheapest. The best oil soluble is the 1.2.4 Xylenol.

Reflux for 4 hours and vacuum distil. An oil-soluble resin is obtained which hardens when heated further.

The use of acid catalysts gives permanently fusible resins which have high solubility. These resins are very hard, have high melting points, and have high solubility.

TABLE 38

LEADING PHENOLS USED FOR MAKING OIL SOLUBLE RESINS

		M.P. Resin With Formaldehyde (Acid Catalyst)
1.2.4 Xylenol		72° C.
p-tertiary Butyl Phenol		96° C.
p-tertiary Amyl Phenol		58° C.
p-tertiary Octyl Phenol		91° C.
p-phenyl phenol		110°C.

The following examples illustrate the use of acid catalysts in the formation of suitable resins:[9]

(*a*) 61 parts 1.2.4 xylenol (1 mol.)
40 parts formalin (1 mol.)

are refluxed with 3 parts conc. HCl for 4 hours, washed free from acid and vacuum distilled at 120°C.

(*b*) 25 parts p-tertiary butyl alcohol
13 parts formalin

representing 1 mol. equivalent of each are refluxed with 40·5 parts conc. HCl for 4 hours. The solution is then distilled under vacuum at 120°C.

(*c*) 164 parts p-tertiary amyl alcohol (1 mol.)
84 parts formaldehyde (0·8 mol.)

are refluxed with 4·5 parts conc. HCl for 2 hours, washed free from acid and distilled under vacuum at 120° C.

In principle, where the substituent groups contain much oxygen they reduce the oil solubility. On the other hand, they aid the resins to react with glycerol and find a use for combination with alkyd resins. These resins, when incorporated into oils, give varnishes having many attractive characteristics. They have high resistance to climatic conditions, moisture, acids, and alkalis. They have good durability and they aid rapid drying. Turkington and Allen described work successfully carried out on a basis of the addition of 100 parts of resin to 200 parts of tung oil.

In general it has been shown that solubility in oils is increased where the size of the substituent group is increased.

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REFERENCES

1 Bakelite G.M.B.H. B.P. 349,931/1930.
2 BEREND AND ALBERT. B.P. 1,269/1912.
3 BEREND. B.P. 107,205/1916.
4 BRITTAIN. *Ind. Eng. Chem.*, 1941, **33**, 965.
5 BROWN. U.S.P. 1,212,738/1917.
6 BYCK. B.P. 267,736/1926.
7 Catacol. Literature of Catalin Ltd.
8 DE BRUYNE. *Wood*, March 1940.
9 I.C.I. Ltd. B.P. 401,290/1933.
10 TURKINGTON AND ALLEN. *Ind. Eng. Chem.*, 1941, **33**, 966; U.S.P. 1,800,195.
11 Porous Castings. Literature of Bakelite, Ltd,
12 C.I.O.S. XXXIII-23, p. 60.

CHAPTER VI

MOULDING POWDERS

UP to the present time by far the greatest amount of plastics have been used as moulded articles. The most important moulding plastic has been, and unquestionably is still, moulding powder based on phenol-formaldehyde resin. The principles involved in making mouldings from these apply generally to all thermosetting materials, although details may differ.

General Properties of Phenolic Moulding Powders. Products which have been obtained by moulding phenolic resins have an exceptional range of desirable characteristics. They have high mechanical and electrical properties, and are extremely hard. In addition, they withstand high temperatures. With suitable fillers the impact resistance is also of a very high order in relation to other materials. From the chemical point of view the products are extremely inert. Mouldings do not tend to change with age, there is no change of dimensions, nor in any of the characteristic features. They are resistant to oil, grease, etc., and to all the common solvents. They withstand weak alkalis and organic and dilute mineral acids. They do not affect metal inserts. They are extremely resistant to moisture, and this property is substantially improved by the use of suitable fillers. The products are disintegrated by strong nitric acid, sulphuric acid, or strong alkalis.

In view of this range of properties certain important industries have led in the widespread use of phenolic products. For example, the car industry found that they solved many of their problems, particularly in the electrical system. Phenol-formaldehyde articles had just the right combination of properties; first, good electrical characteristics; secondly, because of the high resistance to heat, water, and oils, and also because of the important property of accurate reproduction.

It is fairly evident that the moulded phenolic materials would appeal especially to the electrical industry, which is an enormous consumer of them in every conceivable form. Thus phenolic resins early solved the problem of making available vast quantities of accessories for the radio industry. Again, because of the high corrosion resistance, and impact resistance, they have attained great popularity in the chemical industry.

Phenolic resins, as ordinarily prepared, are not very suitable for use alone as moulding materials, being comparatively brittle, and not having great strength. Moreover, they have an inherent dark colour and are not fast to light. To overcome these drawbacks it has been necessary to compound the resins and convert them into moulding powders. When it has been suitably compounded the product is incomparably superior to that obtained from the bare resin. For the production of moulding powders resin is usually mixed with fillers, pigments, lubricants, catalysts, etc. The usual procedure is to make the resin, thereafter adding the requisite amount of filler, such as wood flour, and the quantity of accelerator that may be required.

TABLE 39. Typical Composition

Formula	1 stage	2 stage
Resin . . .	100	100
Wood flour . .	75–80	75
Hexamine . .	—	5–15
Stearic Acid . .	1·5	1·5
Lime . . .	1·5	—
Dyestuff . .	2	2
or		
Pigment . .	15	15

Phenolic moulding powders are prepared in a number of different grades. These depend upon the purpose for which they are to be used. The chief variation is in the type of the filler. By far the greatest proportion, something like 90 per cent of all moulding powders, contains wood flour. This is the cheapest filler available, and, in general, gives a material which is adequate for most purposes.

Rather smaller quantities of other fillers are employed in moulding powders owing to mixing difficulties.

The usual type of lubricating material is stearic acid. This is widely used because it prevents the sticking of moulding to the mould surface and facilitates ejection of the moulding. Since speed of setting is of primary importance in moulding, it is desirable to prepare the moulding powder so that while it still retains enough flow to enter every part of a mould, it will thereafter set hard as rapidly as possible. The function of the catalyst or accelerator is to carry the degree of set or the *cure* as far forward as is practicable. Small quantities of lime or magnesia are generally used. For two-stage resins hexamethylene tetramine is usually added to provide the necessary additional formaldehyde.

The production of coloured phenolic resins has in the past been somewhat difficult. It has been evident that the colour range was somewhat limited. The reasons are that high temperatures are involved in moulding and the constituents of resins are corrosive and calculated to give dark materials. So that the use of organic dyes until recently has not been too effective. Improvements in this connection have greatly increased the colour range of phenolic moulding powders. In the past inorganic pigments, such as red iron oxide, burnt sienna, umbers, and so on, have been extensively employed.

So far as the resins themselves are concerned, cresylic resins have been most widely used for black and dark brown materials, while for coloured articles phenolic resins have generally been employed.

Pigments and Dyestuffs. The colouring material used with phenolic resins and indeed for most plastics, are similar in many respects to those used for rubber and paints. The characteristics required for materials used to colour thermosetting plastics are good tinting power, hiding power, fastness to light, resistance to high temperature and chemical attack. In a great measure the inorganic types also act as filling materials.

Titanium dioxide is, of course, the leading white pigment. It has five times the whitening power of any other material. Comparatively small loadings are required. It is relatively expensive. A mixture of titanium dioxide and barium sulphide is known as titanium white and gives exceptionally effective white at much lower cost.

Zinc oxide is one of the most widely used white pigments. Among plastics it is chiefly used for casein and ethyl cellulose. It must not be used on polyvinyl compositions. Another suitable white pigment is lithopone which is based on barium sulphate and zinc sulphide.

Then there is the group of fillers which give more or less white compositions; namely, chalk or whiting, alumina, and barytes. Chalk or calcium carbonate is affected by acids which impose limitations on its use. Barytes, which is barium sulphate, stands up to the strongest acids, but is very heavy, having specific gravity of 4·5.

Carbon in one form or another supplies practically all the black pigments and fillers. There are many types available depending on the source and the method of formation. They differ appreciably in particle size, hardness, intensity of colour, and so on. Hard carbon blacks are made by the Channel process of burning natural gas. Thermatomic processes, i.e. cracking, give softer blacks of larger particle size and having less covering power. Then there are lamp blacks and acetylene black which are softer still and have much larger particle size.

Carbon black and the other blacks have not yet acquired anything like the same significance for plastics as they have for rubber. However, I think they will in due course become much more important than they are.

Different Types of Carbon Black. There are four leading types of carbon black:

1. *Channel Black or Gas Black.* This is regarded as the outstanding filler from the point of view of improving rubber properties. It is made by incomplete combustion of natural gas. The flames of burning gas impinge on metal surfaces, and the black deposits. Owing to their extreme fineness the size of the particles has not yet been satisfactorily determined. While Green[3] considered the average diameter as 0·15μ (μ=1/1,000 millimetre), Grenquist[4] placed the diameter in the range between 15μ to 200mμ (1mμ=1/1,000,000th millimetre).

2. *Acetylene Black.* This is produced by the explosive combustion of purified acetylene in closed chambers. Comparatively little work has been carried out to determine its particle size, which is thought to range between carbon black and lamp black.

3. *Lamp Black.* This is obtained by incomplete combustion of fats, oils, tars, etc. Its particle size, according to Green (loc. cit.), is mainly between 0·3μ and 0·4μ, and goes up as high as 1μ.

4. *Thermatomic Black.* Thermal decomposition, or cracking of natural gas in the absence of air, yields thermatomic black. It is said to be about 1μ in particle size.

The particle size is important because of the implication of the surface area generated. Cranor[2] has shown this in terms of acres of surface available per pound of black.

TABLE 40

Type (Carbon Pigment)	Surface (Acres per pound)	Examples
Coarse thermal	1·0	Thermax, Shell, etc.
Fine thermal	4·0	P-33
Semi-re-enforcing ("S.R.") .	3·5–4·0	Furnex, Gastex, etc.
Channel impingement		
Coarse channel . . .	10·3 or less	Micronex W-6, etc.
Medium channel . . .	10·5–10·75	Standard Micronex, etc.
Fine channel . . .	11·5–12·0	Micronex Mark II, etc.

Since black mouldings predominate for electrical applications, the poor electrical characteristics of carbon particles has been of some significance, since they might contribute to tracking and similar undesirable effects. As a consequence, black dyestuffs, such as nigrosine and chlorazole, etc., have been widely used.

On the other hand, it should be emphasised that particularly with some thermoplastics having rubbery characteristics, carbon black enhances tensile strength, abrasion resistance, and other physical properties.

A certain number of inorganic colours are extensively employed. Iron oxides of one type or another have supplied red and brown shades. More intense reds are obtainable with mercury sulphide, vermilion or antimony sulphide. Ultramarine and prussian blue provide blue shades. The numerous chrome derivatives provide yellows, greens, and a whole range of other colours.

Dyestuffs predominate for imparting colour to plastics. Where transparent and translucent effects are sought, resin-soluble dyestuffs are invariably employed. The most widely used group are the lake dyes which are used in the same way as inorganic pigments or fillers.

It is quite clear that the chemical behaviour of a filler or pigment must be carefully considered before it is incorporated into a plastic, so that any materials which are affected by acids, for example, should not be used for making plastic compositions which have any chance of coming into contact with acid conditions. Similar limitations should be observed where other usage factors are concerned.

Fillers for Phenolic Resins. The use of fillers has been found to overcome the brittle nature of the pure resins. The nature of the filler used is of considerable importance, for it affects not only the flow characteristics of the moulding powder, but also the general properties of the finished article. The main requirements of fillers are as follows:

(*a*) Good tensile strength and impact strength.
(*b*) Low moisture absorption.
(*c*) Low specific gravity.
(*d*) The ability to be easily wetted by resins and dyes.
(*e*) Cheapness and availability.

Other characteristics which are of value include good electrical properties, light colour, ability to withstand high temperature and chemicals, resistance to acids, alkalis, and solvents, good heat resistance, non-inflammability, and lack of odour or taste. The filler also plays an important part in finishing operations, e.g. drilling, tapping or tumbling, etc.

Wood Flour. The most widely used filler is wood flour. In the past this has been present in more than 90 per cent of all phenolic moulded articles. It is usually employed between 80 and 120 mesh sizes. It is the basis of general purpose moulding powders. The amount employed is normally equal to the weight of the resin, constituting

TABLE 41

PRINCIPAL FILLERS

	Fibrous	Non-Fibrous
Organic Materials— Cellulose types	Cotton powder, flock and fabric Wood flour, sawdust Paper and wood pulp Linen, fibre and fabric Rayon, fibre and fabric Jute, hemp and sisal as thread, string and cord	
Non-cellulosic types	Cork dust and powder Leather dust Wool and wool felt Cottonseed hulls	
Inorganic Materials—	Asbestos Mica Glass fibre	Barytes Slate powder Marble dust Zinc oxide Sulphur Stearite China Clay Talc Pumice Powder Carborundum Carbon black, etc. Graphite Silica Calcium Sulphate Coke dust Kieselguhr
Miscellaneous Materials—	Flour, soya flour, casein, zein, Irish moss, lignin, peat, bone meal, natural gums, walnut shell flour, etc.	

about 45 per cent of the finished moulding powder. Greater proportions have been incorporated in cheap articles.

Although large quantities of wood particles are obtained in normal wood-working processes, it has been found that superior results are obtained by preparing the wood flour by attrition methods. It is found that a grinding process gives rod-like particles of wood which are superior to the shapeless particles otherwise obtained. Quite apart from the mesh size, any sample of wood flour is a mixture of particles of widely varying shapes and sizes. Average length of the individual wood fibre is from 0·002 to 0·007 inches.

According to Redfarn[6] the rod-like particles are thought to give easy flow to the moulding powder because the particles of filler are able to roll over one another.

Wood flour gives good properties to the final product and is quite adequate for most general utility purposes having the necessary physical strength and electrical properties. It reduces shrinkage on cooling. It equalises stresses set up in moulding, etc. It provides anchorage and ability to withstand shock and vibration. Although not the ideal filler, yet its range of properties combined with the enormous quantity always available and low cost guarantee its continued leading position.

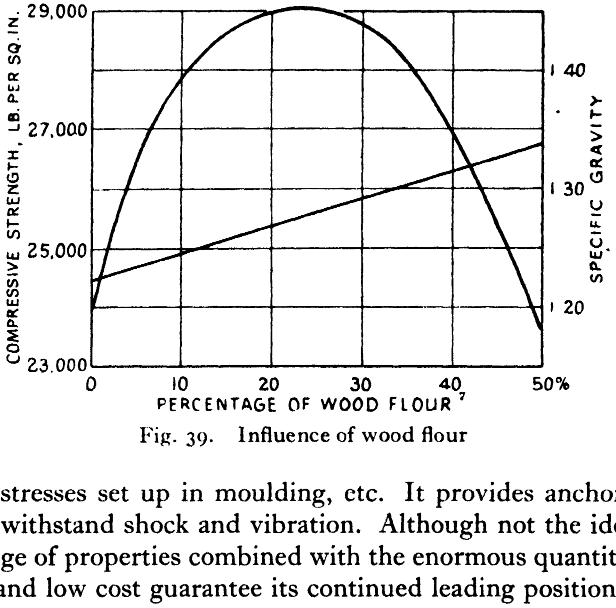


Fig. 39. Influence of wood flour

The leading types of wood flour are light in colour and do not contain appreciable quantities of soluble constituents. Typical commercial varieties are obtained from pine, fir, spruce, and poplar. In the past, most supplies for Great Britain have come from Scandinavia, and were mainly pine.

The relative lightness of wood as a filler has been one of its outstanding characteristics, and also the fact that an excellent finish is obtained. A variation on this theme is the use of powdered nut-shells as filler. A type which has acquired popularity in the United States is ground walnut-shells. By virtue of the hardness of these materials they can more readily be ground to a uniform condition.

It is absolutely essential that wood flour should be dry before being utilised as a filler for phenolic resins. In the ordinary way it contains about 6 per cent water, but it will readily take up much higher amounts. If this is not done, then the moisture present may result in porous products which are unsatisfactory. Particularly where electrical products are to be made, this is a matter of great importance.

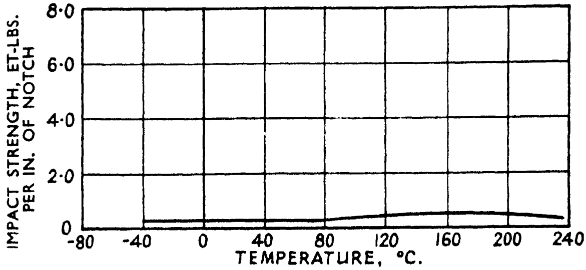


Fig. 40. Impact strength of wood flour filled phenolic moulding

TABLE 42

RE-ABSORPTION OF MOISTURE BY DRY WOOD FLOUR—TYPICAL VALUES FOR VARIOUS HUMIDITIES[5]

Per cent Water re-absorbed during Exposure	Per cent Humidity at 20° C.		
	50%	75%	100%
¼ hour	2·9	4·9	8·4
½ hour	3·9	6·7	10·6
1 hour	4·0	8·5	12·2
2 hours	(Constant weight)	9·0	14·5
4 hours	—	9·6	16·1
7 hours	—	9·9	17·5
20 hours	—	(Constant weight)	—
24 hours	—	—	20·5 (Constant weight)

Frequently it is essential to bake wood flour under controlled conditions to remove moisture.

Moulding powders containing wood flour fillers readily soften and flow under suitable heat and pressure. This enables them to be formed in steel moulds into an endless variety of articles. Their applications may be grouped under the following heads:

(*a*) As standard materials for ordinary electrical and mechanical applications. They are used for car insulating parts, and for decorative parts. Most moulded articles are made from this material.

(*b*) They are widely used for bottle-caps and closures of every description.

(*c*) Such filled materials are specially suited for moulding around inserts.

(*d*) They are widely used as materials for making buttons and ornamental articles.

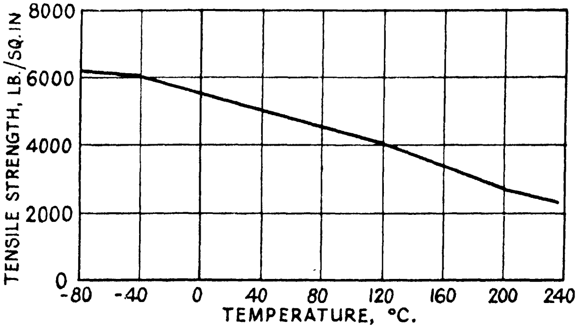


Fig. 41. Tensile strength of wood flour filled phenolic moulding

Fibrous Materials. For many purposes phenolic resins filled with wood flour, although of general and wide utility, still lack impact strength. As a consequence, where impact resistance is of particular importance, other types of fillers are employed. In such cases fillers based on paper, cotton, and other fibrous materials are used. As compared with wood flour, such fillers offer advantages not only in impact resistance, but also in resistance to moisture, resistance to acid, lack of odour, etc. For high impact strength, particles of fabric are outstanding and have come into wide use.

Two main types of cotton products are employed for moulding powders, fabric fillers, and cotton flock. Fabric is cut up into small particles and is available in as many forms as there are woven fabrics, that is to say, from light cottons up to heavy canvas. Cotton flock is obtained by breaking down cotton rags. The outstanding advantage of all these materials is the superior strength of the product. This may be due to interlocking of the woven fibres with phenolic resin. A disadvantage in their use is that such moulding powders have a much greater volume than other materials which can pack more closely.

Other fibrous materials are coming into use. The fibres used for cords and strings, such as sisal, manilla, jute, etc., have found expanding application for reinforcing resins. Such fibres give results which have proved even superior to fabric particles and flock. While these fibrous materials confer shock-resisting characteristics, they are rather more difficult to mould because the filler impedes the free flow of the material.

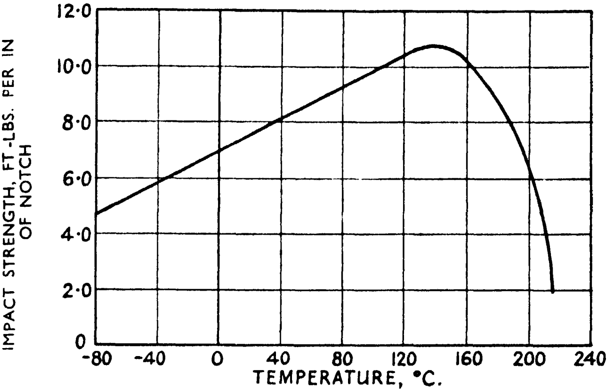


Fig. 42. Impact strength of shock-resisting phenolic moulding

Sisal, in particular, is already extensively used. Resin-bonded sisal offers many advantages. The sisal is worked up into a consolidated felt. This is impregnated or treated with resin, rough shapes cut and then moulded. Only comparatively flat and simple mouldings are practicable

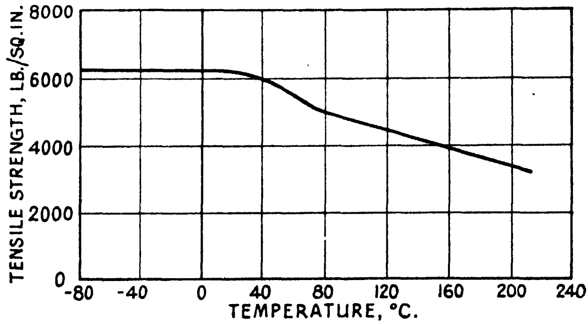


Fig. 43. Tensile strength of impact grade phenolic moulding

since there is little flow. Pre-cut shapes are essential. Very high impact resistance and low-density mouldings are obtained. The material is used for articles where high impact strength is desired.

Outstanding examples of shock-resisting materials include telephone sets, tool housings, and instrument housings of various types. Vacuum-cleaner parts, washing-machine parts, etc., are other examples which are usually moulded from shock-resisting phenolic materials.

Filler made from nutshells are finding commercial application. The leading types are walnut shell flour and coconut shell flour.

TABLE 43

SPECIFIC VOLUME OF FILLERS

	Specific Gravity	Specific Volume (No. of c.cs. occupied by 1 gram)
Carbon-black	1·8	0·555
Zinc oxide	5·6	0·179
Whiting	2·7	0·370
Clay	2·6	0·385
Lithopone	4·1	0·246

Mineral Fillers. The fillers already described give mouldings which have had adequate heat resistance for most applications, yet there are many uses where a much higher resistance to heat is desirable. Where outstanding heat resistance and also superior water resistance are required, fillers such as asbestos fibres and powdered mineral materials are employed. Desirable features which all fillers should possess are:

(*a*) Fine and regular particle size.
(*b*) Absence of gritty particles.
(*c*) Absence of moisture.

TABLE 44

THE INFLUENCE OF FILLER ON MOULDINGS

	Nature of Filler						
	50% Wood flour	25% Wood flour 25% Silica	50% Mica	50% Asbestos	Fabric Filled	Cotton Flock	Heavy Cord
Tensile strength, lb./sq. in.	9,000	8,000	8,000	6,000	7,500	8,000	9,000
Compressive strength, lb./sq. in. . .	22,000	25,000	19,000	17,000	—	—	—
Flexural strength, lb./sq. in.	8,000	9,250	8,500	6,700	11,000	9,000	13,000
Impact strength, ft./lb. per inch of notch .	2·0	1·65	1·35	1·5	3	1·25	8·0
Water absorption (24 hours at 20°C.) .	0·50	0·50	0·05	0·25	0·8	0·65	0·8
Specific gravity .	1·35	1·50	1·75	1·90	1·35	1·38	1·36

Widely used mineral fillers include diatomaceous silica, powdered mica, talc, clay, whiting, barytes, etc. It is also a fact that mineral fillers have more uniform particles than have the organic fillers. Such

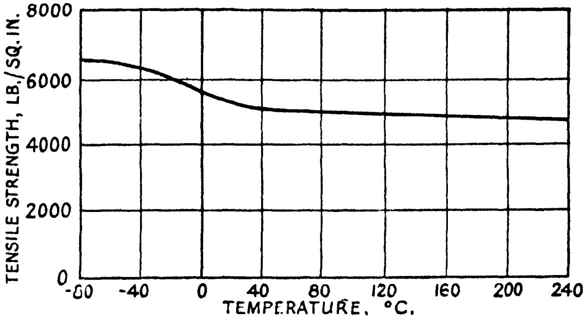


Fig. 44. Tensile strength of heat-resisting phenolic moulding

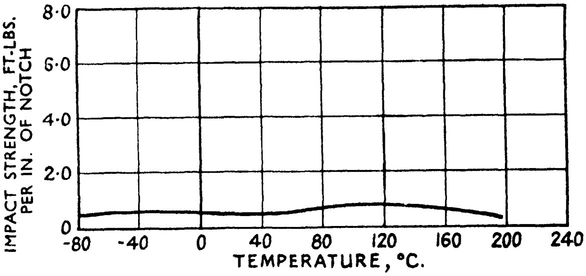


Fig. 45. Impact strength of heat-resisting phenolic moulding

TABLE 45

APPARENT SURFACE OF FILLERS[9]

	Apparent Surface (sq. in. per c. in.)
Carbon-black	1,905,000
Lamp-black	1,524,000
China clay	304,800
Ferric oxide	152,400
Zinc oxide	152,400
Glue	152,400
Lithopone	101,600
Whiting	60,950
Fossil flour	50,800
Barytes	30,480

TABLE 46

CHARACTERISTICS OF SOME TYPICAL THERMOSETTING MOULDING POWDERS (PHENOL-FORMALDEHYDE TYPE)[5]

Sample No.	1	2	3	4	5	6
Colour	Brown	Grey	Black	Black	Black	Yellow
Analysis—per cent:						
Phenolic resin	49·5	38·0	53·5	53·5	60·5	35·0
Wood flour (dry basis)	37·5	41·5	35·7	39·5	32·0	Nil
Moisture	4·5	4·0	4·3	5·0	5·5	1·0
Mineral pigment or filler	8·5	16·5	6·5	2·0	2·0	64·0
	100·0	100·0	100·0	100·0	100·0	100·0
Nature of colourant	Oxide of iron	Carbon black	Spirit soluble dye	Spirit soluble dye	Spirit soluble dye	—
Nature of mineral matter	Oxide of iron	China clay	Oxide of iron	—	—	Clay
Specific gravity of moulding powder	1·17	1·23	1·15	1·20	1·15	1·28
Particle size—per cent:						
Retained on 20 mesh	30	4	30	30	25	5
Passing 20, retained on 40 mesh	30	32	30	35	30	25
Passing 40, retained on 100 mesh	20	34	20	20	25	30
Passing 100, retained on 200 mesh	10	16	10	10	10	25
Passing 200	10	14	10	5	10	15

materials have another important advantage over the organic fillers because they have a lower coefficient of expansion. This is a matter of considerable importance when the problem of accurate dimensions is involved. Often both fibrous and mineral fillers are used together.

Specific gravity of fillers is important. Heavy fillers are at a disadvantage, e.g. litharge 9·3, and zinc oxide 5·6. At the other end of the scale are kieselguhr 2·2, clay 2·6, carbon black 1·8.

Fig. 46. A typical heavy duty article moulded from phenol-formaldehyde moulding powder[10]

Mineral fillers give moulding powders which have poor flow characteristics; the products also offer more resistance to subsequent machining. By virtue of these working difficulties, smaller proportions of the fillers are employed than is the case with the cellulose fibres. While more difficult to process, and not flowing so readily as the wood-flour type, on the other hand they give far superior heat resistance and water resistance. Applications where such materials are employed include heater connections, handles of cooking utensils, heater plugs for irons, etc.

The tensile strength of mouldings made with mineral fillers is lower than with wood flour and fibrous fillers. This is because they are not easily wetted by the resin and consequently give relatively poor anchorage. Diatomaceous silica seems to be one of the best, and it confers such properties as resistance to water, low specific gravity, low power factor, good colour possibilities, and good flow. Kieselguhr, infusorial earth, and fossil flour are other leading diatomaceous materials. Owing to their shell-like shape they are somewhat absorbent. Actually they are the finely divided silica remains of diatoms and other organisms. They are completely inert, resist heat, steam and chemical attack, and are used as fillers for phenolic resins and many of the thermoplastic materials. They also find some application in preparing light-coloured aminoplastics.

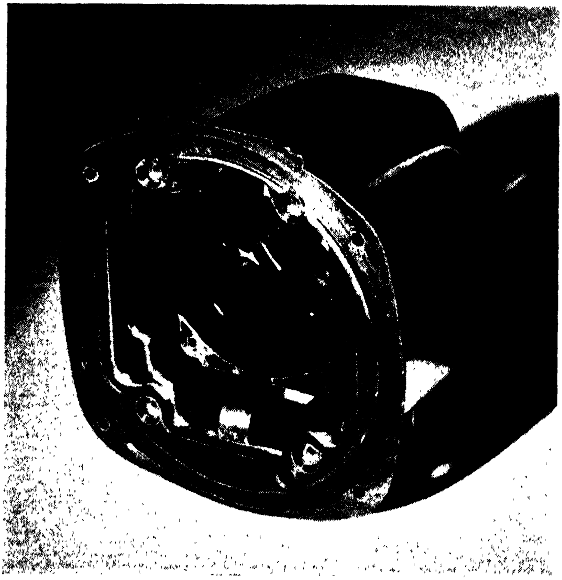


Fig. 47. Moulded motor housing of the Hoover Junior vacuum cleaner[10]

Asbestos is widely used as a filler for the preparation of materials which have to withstand chemicals and corrosion.

Other specialised materials are utilised for specific products. Special consideration has to be given in the preparation of moulding powders for products which have to be used in contact with chemicals as accessories for textile machinery, rayon spinning, and chemical plant generally. Special low loss moulding powders have been developed for electrical requirements. In fact, a whole range of exacting industrial requirements may be fulfilled by variation in the types of fillers.

TABLE 47

THERMAL CONDUCTIVITY OF FILLERS[1]

Ingredient	Thermal Conductivity cal. cm./cm.^{2} °C. sec.
Zinc oxide	·00167
Iron oxide	·00132
China clay	·00106
Lithopone	·00092
Blanc-fixe	·00078
Whiting	·00084
Talc	·00090
Magnesium carbonate	·00057
Carbon-black	·00066
Lamp-black	·00140
Graphite Acheson	·00217

Mica. Mica as a fine powder is widely used as a filler, particularly for phenolic moulding powders. There are difficulties in mixing it, and other fillers are generally employed together with it. By virtue of its flat plate-like form there is evident a tendency for lamination in

TABLE 48

SUMMARY OF DATA UPON MICA[5]

	Muscovite group	Phlogocite group
General name	Potash or white mica	Amber mica or magnesia mica
Chief source	India	Canada
Chemical analysis (typical) %:		
Silica	45·2	40·8
Alumina	38·4	26·9
Potash	11·8	12·7
Magnesia	—	7·6
Ferric oxide	—	12·0
Water	4·6	—
Specific gravity	2·75–3·0	2·75–2·85
Moh's hardness	2·8–3·2	2·5–2·7
Max. safe working temperature	500° C.	1,000° C.
Permittivity	4·2–5·0	2·9–3·0
Specific resistance, ohms × 10^{12}	10–100	0·5–20
Electric strength, volts/mil. at 20° C.	3,000–6,000	3,500–4,500
Loss of water % upon ignition at		
450° C.	0·03	Nil
650° C.	0·06	Nil
750° C.	1·69	Nil
800° C.	3·29	Nil
900° C.	4·20	0·20
1,100° C.	4·30	1·0 max.

the moulded article. Moulding powders containing it tend to stick during moulding. It is generally employed for electrical mouldings. It should be noted that mica is one of the leading fillers for shellac.

Finely ground slate powder is also widely used. Its advantages are the inertness and its low cost. Specific gravity is 2·75.

Powdered silica is notably resistant to acid. As a consequence it is used as a filler for phenolic resins which are to be used in chemical equipment. China clays, kaolin, etc., are used as fillers for plastics, augmenting the use of wood flour in many instances. They are resistant to chemical influences. Another notable inorganic material is talc (hydrated magnesium silicate), which is also widely used as a filler.

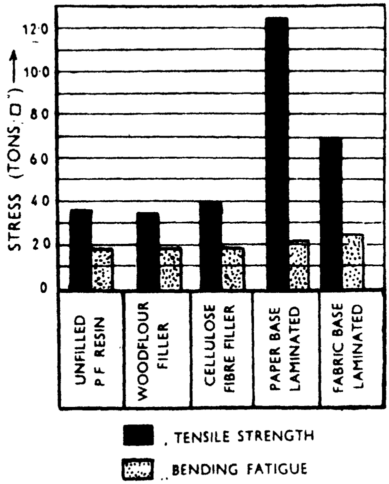


Fig. 48. Influence of types of fillers on properties[8]

Asbestos. Asbestos is used as a non-inflammable fibrous filler. It gives mouldings which will withstand much higher temperatures than those containing wood flour, cotton, etc. It does not give such high mechanical strength. Its leading application is in phenolic compositions. It is the filler used in *Haveg and Keebush* phenolic compositions designed for chemical engineering equipment, etc.

Asbestos varies according to the source from which it derives, being available as long fibres or short fibres. The blue types come from India and South Africa, the white from Canada. Long fibres will look better, but are mechanically weaker. The fibres are relatively weak, so that the normal mixing procedure tends to break the fibres down. Hence, when the full strength is desired great care is necessary in mixing. Asbestos is only wetted with difficulty by phenolic resin, so that often a wet mixing process is employed using a solution of phenolic resin, the solvent being subsequently removed by heat. In this manner the fibrous character is retained.

TABLE 49

SUMMARY OF DATA UPON ASBESTOS

Average Characteristics	Mineral Group	
	Amphibole	Serpentine
General colour of fibre	Bluish lavender	White
Nature of fibre	Springy, harsh	Soft and silky
Specific gravity, average	3·25	2·25
Strength, tension	Poor	Good
Strength, flexing	Poor	Good
Solubility in acid, average (hydrochloric)	10%	60%
Critical temperature	300°C.	400°C.
Iron content	0 to 35%	Very low

Asbestos is generally regarded as a fire-resisting substance, but this is not entirely true. When in contact with a flame asbestos does not burn, but the flame temperature does destroy, to a large extent, the physical strength of the fibres. White asbestos will stand temperatures up to 400°C. and blue asbestos 300°C. before the physical strength is affected.

White asbestos is readily attacked by mineral acids, but blue asbestos is much more resistant, although it is attacked to some extent.

White and blue asbestos differ considerably in weight, the specific gravities being white 2·3, blue 3·2.

White asbestos has a greater tensile strength than blue asbestos, and is not so harsh and brittle, so it can be more readily spun into threads for weaving.

Asbestos readily absorbs an appreciable amount of moisture, but in plastic compositions, for example, asbestos-filled phenolic mouldings, the resin component waterproofs the composition, whilst the asbestos gives it increased heat resistance.

The Preparation of Moulding Powders. Phenolic resin has to be mixed with the other components. Mixing is either carried out in an internal mixer, such as the Banbury mixer, or on open rolls, such as the mixing mills commonly employed in the rubber industry.

Internal mixers are extensively employed for every type of plastic.

TABLE 50

CHARACTERISTICS OF TYPICAL PHENOL-FORMALDEHYDE MOULDINGS[5]

Group	Colour	Ash, %	Nature of pigment and mineral filler	Specific gravity at 20°C.	Acetone soluble matter, %	Water absorption (24 hrs. at 20°C.), %	Loss on heating (6 hrs. at 110°C.), %	General type
Ordinary wood filled . .	Black	2·3	Lake dyestuff	1·32	3·7	0·28	0·30	Wood flour filled, electrical quality
Ordinary wood filled . .	Black	3·7	Lake dyestuff	1·31	3·8	0·31	0·50	Wood flour filled, electrical quality
General coloured mouldings .	Green	7·0	Calcium lake pigment, china clay filler	1·45	10·0	1·0	2·4	Wood flour and mineral filled
General coloured mouldings .	Red	10·0	Lake dyestuff, lithopone pigment	1·46	4·0	0·15	0·55	Wood flour and mineral filled
General coloured mouldings .	Black	12·0	Lake dyestuff, clay filler	1·35	3·0	0·80	1·58	Wood flour and mineral filled
General coloured mouldings .	Red	7·0	Red iron oxide, aluminium oxide	1·35	8·5	0·70	1·80	Wood flour and mineral filled
General coloured mouldings .	Red-brown	10·0	Red iron oxide, aluminium oxide	1·45	4·5	0·20	0·40	Wood flour and mineral filled
General coloured mouldings .	Mottled red	7·5	Lake black pigment, mercury sulphide pigment, iron and aluminium oxides	1·40	6·0	0·28	0·80	Wood flour and mineral filled

General coloured mouldings	Nutbrown	7·0	Iron and aluminium oxides	1·35	7·5	0·28	0·45	Wood flour and mineral filled
General coloured mouldings	Yellow-brown	2·7	Dyestuff	1·45	5·8	0·57	1·43	Wood flour filled, no mineral colourant
Shock resistance	Black	1·3	Lake dyestuff	1·25	3·5	0·38	0·65	Cotton flock filled
Shock resistance	Black	2·0	Lake dyestuff	1·35	5·5	0·20	0·25	Cotton flock and wood flour filled
Shock resistance	Black	8·5	Lake dyestuff, diatomaceous earth filler	1·40	4·0	0·82	0·60	Cotton flock and mineral filled
Fire resistance	Black	26·5	Lake dyestuff, asbestos and diatomaceous earth	1·85	6·6	0·90	0·85	Asbestos and mineral filled
Shock resistance	Black	11·0	Lake dyestuff, china clay filler	1·40	5·9	0·30	0·66	Wood filled and mineral filled
Shock resistance	Natural brown	9·8	Siliceous earth	1·58	5·1	1·05	1·45	Kraft paper and mineral filled
Dimensional stability and electrical properties	Black	60·5	Lake dyestuff, mica filling	1·80	1·9	0·10	0·10	Mica filled, special electrical grade
Dimensional stability under prolonged heat exposure	Yellow	60·7	Clay filler	1·79	1·3	0·15	0·28	Mineral filled, heat resistant
Dimensional stability under prolonged heat exposure	Brown	30·0	Clay filler	1·65	1·5	0·10	0·13	Mineral filled, heat resistant
Dimensional stability under prolonged heat exposure	Natural	36·5	Clay filler	1·65	8·9	0·15	0·39	Mineral filled, heat resistant
Dimensional stability and electrical properties	Black	39·6	Lake dyestuff, mica filling	1·66	3·4	0·08	0·12	Mica filled, special electrical grade
Dimensional stability and electrical properties	Natural	43·8	Mica filling	1·66	3·0	0·10	0·16	Mica filled, special electrical grade

TABLE 51

COMPARATIVE CHARACTERISTICS FOR MOULDED PHENOLICS HAVING DIFFERENT FILLERS

	Type of Filler						
	Normal Wood Filled	Chopped Cotton Cloth, large pieces	Shredded Cotton Cloth	Cotton Linters	Mica	Asbestos	Mineral Powder for Heat Resistance
Mechanical values:							
Impact strength, BSS 771, ft./lb.	0·20	1·0	0·75	0·35	0·20	0·10	0·20
Cross breaking strength, tons/sq. in.	5·0	6·0	5·0	4·5	4·0	3·0	3·0
Tensile strength, tons/sq. in.	3·0	3·0	3·0	3·0	3·0	2·0	2·0
Crushing strength, tons/sq. in.	15·0	14·0	14·0	16·0	10·0	8·0	10·0
Physical values:							
Specific gravity	1·35	1·35	1·35	1·35	1·66	2·0	1·70
Water absorption (24 hrs.), %	0·3	0·5	0·5	0·4	0·1	0·1	0·1
Approx. max. safe temperature, °C.	135	135	135	135	150	160	160
Electrical values:							
Power factor at 800 cycles, %	Up to 40	Up to 40	Up to 30	Up to 30	3	15	15
Electrical strength at 20°C., volts/mil. AC	200	150	150	200	300	200	180
Electric strength at 90°C., volts/mil. AC	50	25	50	250	150	150	100
Permittivity	8·0	8·0	8·0	8·0	6·0	10	15
Volume resistivity at 20°C., ohms/cm. cube	10^{12}	10^{10}	10^{11}	10^{11}	10^{13}	10^{12}	10^{11}

For very rapid and convenient mixing one of the most widely used machines is the Banbury.

Fig. 49. Camera moulded from P.F. moulding powder[10]

Fig. 50. Housings for ball bearings moulded from P.F. powder[10]

This consists essentially of an enclosed mixing chamber, which looks like two adjoining cylinders with a ridge at their lower junction. This chamber is jacketed to take steam or water. In each cylinder there is a revolving blade, pear-shaped in cross-section, each of which turns at a different speed. These blades, known as rotors, form a spiral along their length. For mixing plastics the rotors are cored to take steam or water. When the rotors turn the action is to mix every part of the stock thoroughly, this action taking place between the blades and also between each blade and the surface of the chamber. The material is kept in the mixing chamber by means of an air-operated weight in the feeding neck. There is an outlet at the bottom of the machine for removing the treated material. Usually a conveyor belt leads from the Banbury to a set of mixing rolls on which mixing is finished off, and the material may be rolled into sheets if desired.

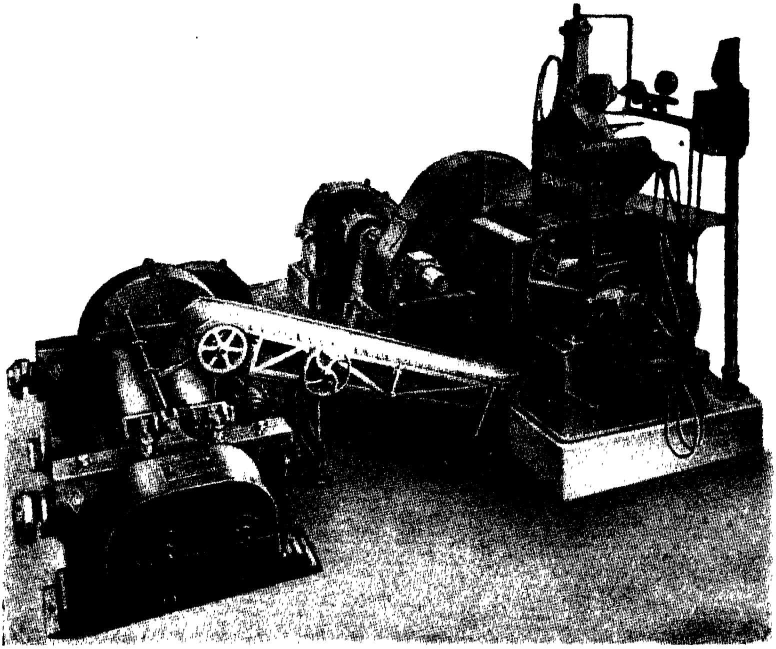


Fig. 51. Banbury mixer, conveyor, and mixing mill[11]

The technical advantages of using an internal mixer are:

(*a*) It converts plastics to a desired degree of plasticity very rapidly.
(*b*) It produces uniformity in mixed materials.
(*c*) There are considerable savings in power.
(*d*) Large quantities of materials may be handled at one time, making control of the mixing easier.

Another feature is that many filling materials which are sometimes difficult and unpleasant to handle are confined to the mixing chamber and prevented from spreading over the establishment.

Mixing Rolls for Plastics. Mixing rolls are widely employed in the production of practically every type of plastic. They closely resemble those that have been used in the rubber industry for a century.

Essentially the machine consists of two adjacent chilled iron rolls placed horizontally, rather like an enormous metal mangle. The rolls are hollow so that they may be cooled by water, or heated by steam, which enters and leaves through special glands. For the actual mixing process the rolls are brought up to a fairly high temperature by high pressure steam. They rotate inwards towards each other.

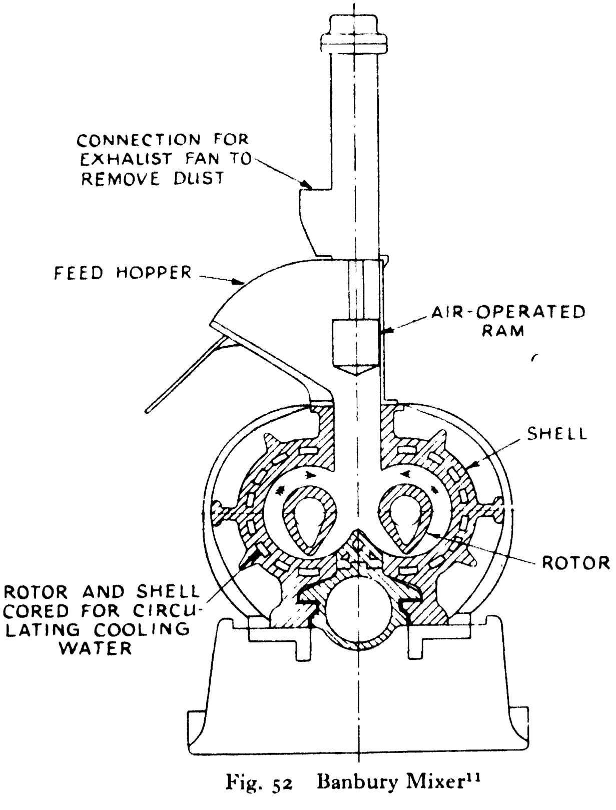


Fig. 52 Banbury Mixer[11]

Hand-operated scrapers are fitted to both rolls, in order that material may be stripped from the rollers when desired.

For mixing purposes the rolls move at different speeds, so that friction is applied to materials being treated, the idea being to smear the plastic around the filler particles and to promote mixing. The back roller is the faster. A normal speed for plastics work is 1·1 to 1.

The distance between the rolls, known as the "nip," may be adjusted by moving the front roll towards or away from the back roll. The tighter the "nip" the more intensive is the mixing. Each roll is driven from gears which are motivated by a high-power motor. A rough rule is that 1 h.p. is required for each 1 inch length of roll, decreasing as the size increases.

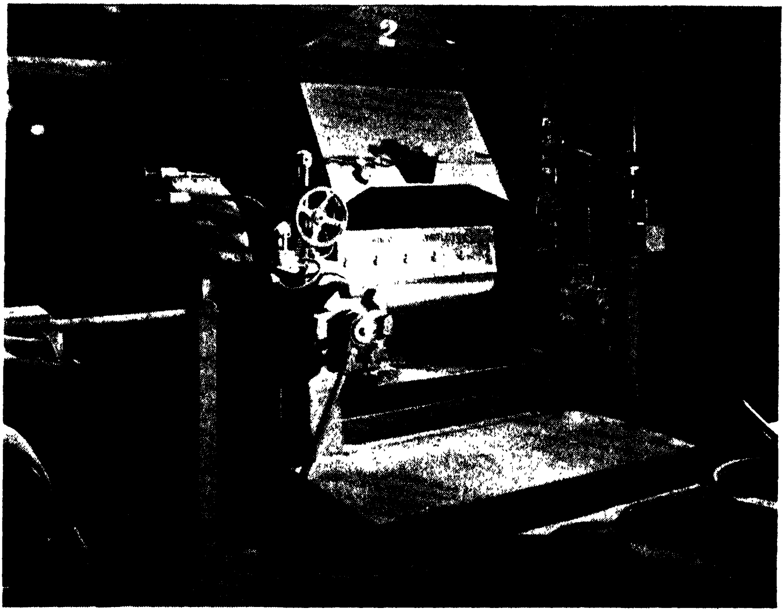


Fig. 53. Typical mixing rolls used for small batches of phenol-formaldehyde moulding powder[12]

The largest machine available has rolls 84 inches by 26 inches diameter, with walls 2 inches thick. A typical machine suitable for plastics has rolls 48 inches long by 16 inches diameter. It is driven by a motor of 40 h.p. The rolls run at a ratio of 1·1 to 1. It can take a batch of about 50 lb. of material having a density of 1·4.

For the handling of plastics in general, the mixing rolls are fitted with a hood, in order to carry off for recovery any solvents that may be used, or any noxious vapours that may be given off at the comparatively high temperatures employed. Temperatures up to 160°C. may be used for various purposes.

The Mixing Procedure for Phenolic Moulding Powders. The material is fed between the rolls. Under the influence of heat the resin portion softens and adheres, forming a blanket round the front roll. A bank of material forms above the join (or nip) between the two rolls. The resin softens and acts as a binder for the other material. A scraper which can be moved against the front roll by the turn of a handle serves to lift the material from the roll surface, so that intimate mixing may be carried out, the mixture being frequently folded across itself. During this procedure the heat generally carries the cure forward. The time of mixing and the temperature used control the extent to which the cure is advanced.

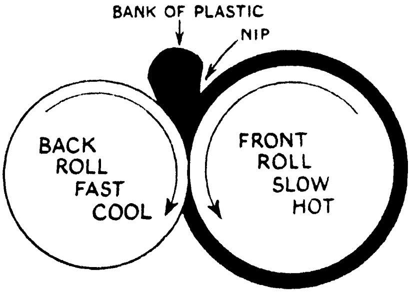


Fig. 54. The mixing rolls

When sufficient mixing has been attained, which may be between 5 and 15 minutes, the material is removed from this machine, as a soft doughy blanket of material. It may be fed on to another similar machine with cooled rolls running at even speeds. Here the blanket is converted almost immediately into a thin board-like sheet, so that further cure is inhibited. This hard sheet is passed into a rotating crusher, and is disintegrated into granules. Successive batches of these may be blended in a large rotating mixer, and the material is then a commercial moulding powder.

Phenolic Moulding Materials. Phenolic moulding powders are made on a large scale at some of the leading German factories.[13] Different methods are used, depending on the types of moulding material being produced. For wood-filled materials two general methods are used:

(*a*) Rolling on mixing rolls.
(*b*) Kneading and rolling.

At one works the resin and hexamethylene tetramine are ground in a hammer mill and mixed with the other constituents in an open Werner and Pfleiderer mixer which is not heated. The batch size is 300 kg. The mixed material is then rolled on mixing rolls. The size of these rolls is 1,000 mm. long and 400 mm. diameter. The normal operating conditions are:

Front roll temperature, 80° C.; speed, 20 r.p.m.
Back roll temperature, 100° C.; speed, 12–15 r.p.m.

The sheet formed is crushed in a toothed crusher and ground in a M.A.G. mill in which there are 12 fixed pegs on the rotating portion which travels normally at 2,500 r.p.m. The material is ground between revolving and fixed pegs and passes through a circumferential screen.

The moulding materials from both processes are finally blended after crushing and grinding. The blending is done in a mixer with two S-type blades, both mounted on the same shaft and both driving the material towards the centre. The blender charge is 1,200–1,400 kg. and actual blending time is 1 hour, the total operation requiring 2 hours.

High Impact Moulding Material. High impact moulding material is made from cut fabric which is impregnated with an alcohol solution. Impregnation is done in an edge runner mill in which the runner wheels are arranged in two pairs and rotate in one direction while the pan rotates in the opposite direction. The discharge is through an opening in the centre of the pan. Side-scrapers assist the discharge of material and the runners are fitted with ploughs. Mixing time is 15 minutes. The material from the mixer is dried in trays in a vacuum oven or in a Simplex drier. The vacuum oven operates at 80°–90°C. at a pressure of 50–70 mm. Hg. Drying time is 8½ hours. The Simplex drier, which is preferred, is semi-automatic in operation. The material on wire mesh trays 38 by 76 by 10 cm., is placed in frames which hold 8 trays (4 kg. per tray). These frames are lifted automatically and fed in at the top of the oven. As one tray is put in, a finished tray is removed from the bottom. The oven contains 10 frames and the drying time is 80–100 minutes.

The oven is heated by steam coils and hot air is blown through the material.

The dried material from the vacuum oven or Simplex drier is passed through toothed rolls to break up the pieces, and is then blended. The blender is a hexagonal tumbler mounted diagonally and rotated at 15–20 r.p.m.

REFERENCES

1 Barnett. *Ind. Eng. Chem.*, 1934, **24**, 303.
2 Cranor. *Rubber Chem. and Tech.*, 1943, **16**, 695.
3 Green. *Chem. Met. Eng.*, 1923, **28**, 53.
4 Grenquist. *Ind. Eng. Chem.*, 1929, **21**, 667.

5 HALLS. *Plastics*, 1942, **6**, 268, 304, 311, 352.
6 REDFARN. *British Plastics*, 1940, **12**, 48.
7 SIMMONDS. *Industrial Plastics.* p. 24. Pitmans Ltd., London, 1940.
8 WARBURTON-BROWN. *Plastics*, 1942, **6**, 218.
9 WIEGAND. *India Rubber World*, 1921, **63**, 425.
10 Illustrations by courtesy of Bakelite, Ltd.
11 „ „ David Bridge & Co., Ltd.
12 „ „ I.C.I. (Plastics) Ltd.
13 C.I.O.S. XXXIII–23, p. 45.

CHAPTER VII

THE MOULDING OF PHENOLIC RESINS

MOULDING of phenolic resins is carried out in steel moulds which are heated and subjected to pressure; at the same time under the heat and pressure the fusible moulding powder is first fluxed and then flows into every part of the mould. It then hardens and sets quite firm. When it has become infusible, the moulding can be removed even while hot, without distortion. As a result of the combination of the pressure and the chemical change caused by the heat, the moulding powder has been transformed into a homogeneous solid. It is fundamentally important that the moulding powder should be dry, otherwise there will be blistering and porosity. There are thus two fundamental characteristics to a moulding powder:

(*a*) The flow behaviour which enables it to fill every crevice in the mould.

(*b*) The time of setting by heat or the "cure," as it is known.

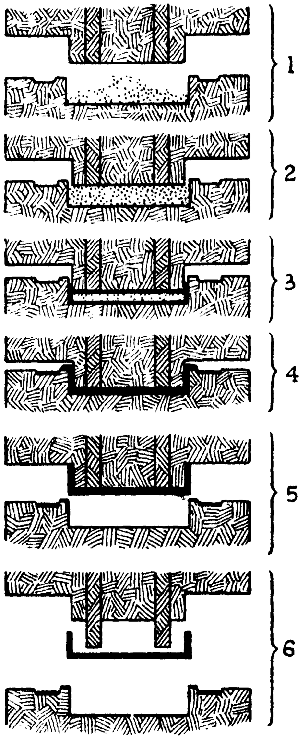


Fig. 55. The moulding operation

The Moulding of Phenolic Resins.

In brief the process of moulding is carried out as follows:

1. Powder is placed in the mould cavity.
2. Hydraulic power presses the lower mould against the upper.
3. The heat, which may be up to 180° C., begins to liquefy the powder.
4. Heat and pressure which may be up to 4 tons per square inch cause the powder to flow, take the shape of the mould, and finally set hard.
5. The plastic sticks to the upper mould.
6. Ejector pins knock the moulded article free.

Advantages of Moulded Phenolic Powders. Moulded phenolic resins have the following leading applications:

1. *When electrical insulation is required,* since they have high dielectric strength.
2. *When moisture and chemical resistance is sought.* They neither warp nor swell when covered by water, and they are not materially affected by weak acids, alkalis, or organic solvents.

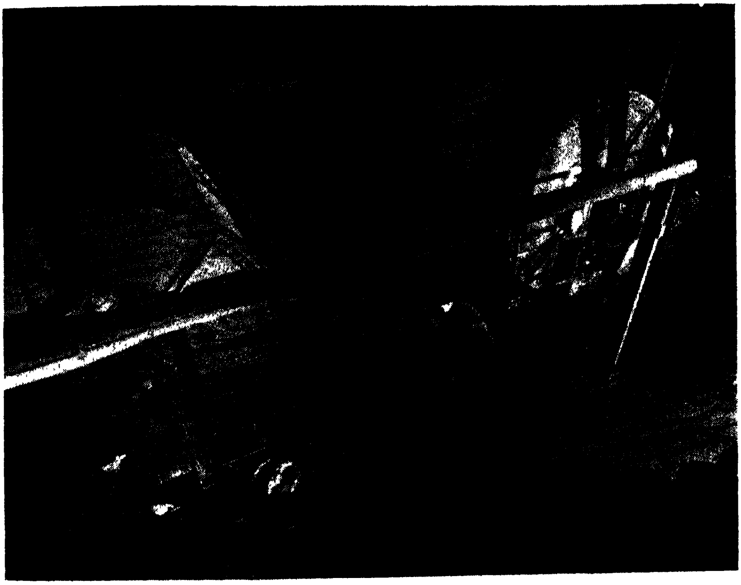


Fig. 56. Rotary premixing machines in which powdered phenolic resins (Novolak) is mixed with hexamethylenetetramine, wood flour, and colouring material[6]

3. *When exposed to wide variations of heat and cold.* These thermosetting resins neither crack at −80°C., nor distort at + 160°C. Tests show that tensile and compressive strengths increase below zero, while impact toughness increases at higher temperatures.
4. *When operating noise is to be reduced and machine vibrations dampened.* They have a degree of resilience which tends to absorb severe vibrations and to cushion repeated shocks.
5. *When a combination of mechanical strength and light weight is essential.* They withstand high-compression loads, pound for pound, better than steel; they flex well without fatigue failure; the flexural strength is high and hysteresis low; and they resist hard impact blows.

The outstanding characteristic of mouldings made with these phenolic powders is the amazing accuracy of the reproduction of every detail. Each article leaves the mould with the exact dimensions. It also reproduces any markings which may be present in the mould surface. This amazing accuracy of reproduction and finish accounts to a great extent for the wide use of phenolic moulding powders.

There are additional factors which greatly enhance the importance of the moulding method. For example, metallic inserts of every kind can be securely embedded as part of the moulding process. Screws, bushes, collars, etc., are invariably embedded in this way. This eliminates expensive assembling operations and finishing, and, indeed, gives a superior product.

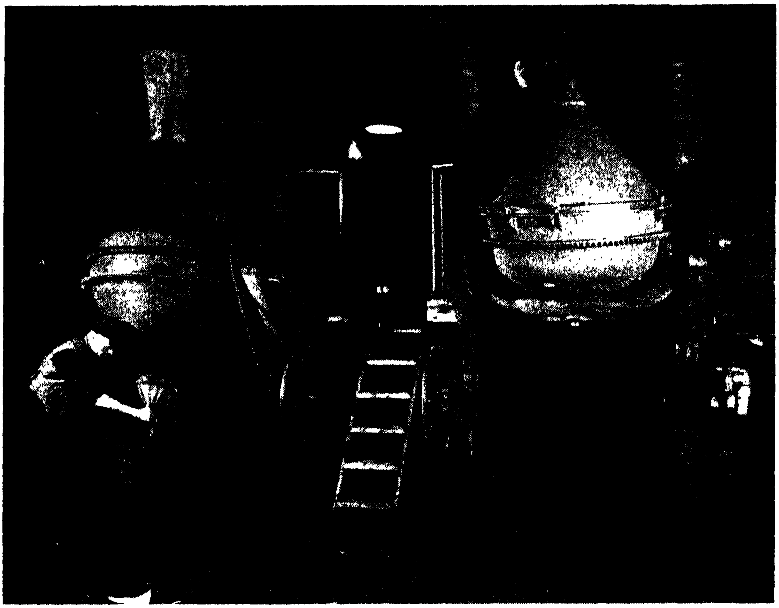


Fig. 57. Small blending machines for the manufacture of small batches of phenol-formaldehyde powder[6]

From the handling point of view, the moulded products can be machined without much difficulty. Tools used for working brass are eminently suitable for handling them. For example, they may be drilled, tapped, threaded, and so on. It is one of the features of the process that in most cases these requirements can be arranged as part of the moulding process. The production of threads of every description is commonplace. The moulded article does not tend to change with age, and is quite permanent in character and dimensions.

Moulding Procedure. There are two methods for moulding phenolic powders: *compression moulding* and *transfer moulding*. In both these methods heat and pressure are employed, but the principle involved is rather different in each instance.

The phenolic moulding powder may be placed in the lower part of the mould, either as a loose powder or as pellets or in the shape of a preform tablet, which may conform roughly to the contour of the mould. Moulding powder is usually poured into the mould from standard measures.

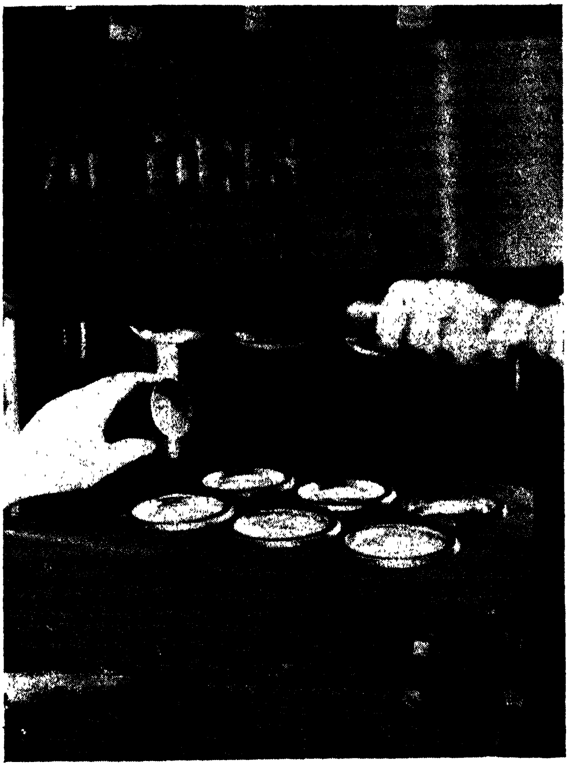


Fig. 58. Filling the mould apertures with powder[4]

Since moulding powder is bulky in relation to the final moulding and to the size of the mould, prior to moulding, the processed material very often is weighed out and formed into a biscuit by cold-moulding. This preformed pellet is known as a *preform*. The preform has a definite weight approximating to that of the final moulding.

Advantage of Preforms. The shape of the preform is made as near as possible to that of the article to be moulded. This process of preforming is used when possible because it greatly hastens production. It decreases the time required to load a multi-cavitied mould. The material is approximately in the ultimate shape and much less flow is necessary. In addition, less material is wasted and there is little danger of contamination when preforms are used.

Fig. 59. Typical shapes of preforms[7]

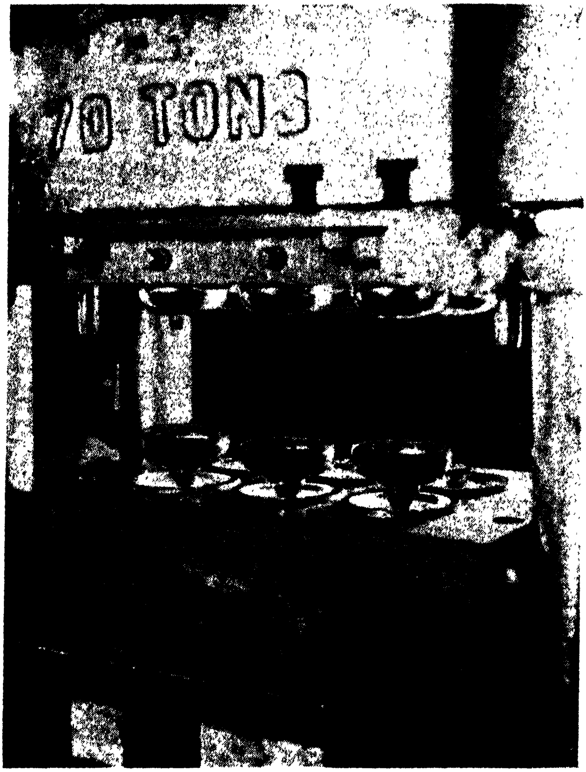


Fig. 60. Ejecting the finished moulding[4]

Preforms are employed where the use of fairly bulky moulding powder is a disadvantage. Powder is difficult to weigh and is awkward to measure with any degree of accuracy. It occupies a great deal of space in the mould and carries entrapped air with it. It was found that phenolic moulding powder could be compacted under pressure in the cold without in any way impairing the plastic processing properties. This led to the technique of preforming. In a sense this resembles the preparation of pills by a pharmacist.

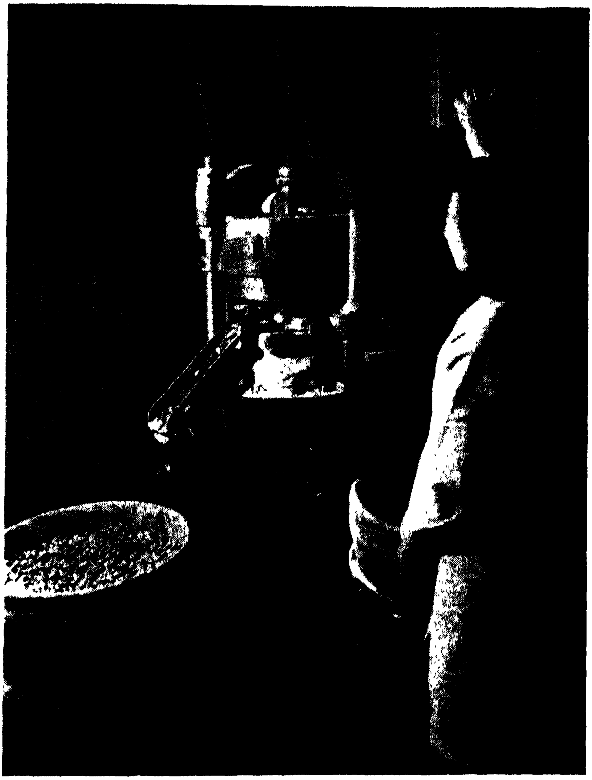


Fig. 61. Pelleting or preforming machine[6]

A measured volume of powder is fed from a hopper into a mould and subjected to pressure. No heating is involved. A preform moulding or pellet is obtained. This is placed in the actual processing mould instead of moulding powder, and the normal moulding procedure is carried through.

Preformed tablets for use as mould charges can be turned out at the rate of 20 to 700 preforms per minute in a special type of press, unheated and specially adapted for this operation. While each preform can be placed by hand in the mould aperture, this becomes awkward and slow where there are a large number of mould openings; for example, in the moulding of bottle-caps. In such cases the usual procedure is to have a frame with apertures corresponding to the mould openings. A removable board is fitted beneath the frame which is filled with preforms, and placed over the mould in the press. The removable board is withdrawn and each pellet drops into its aperture. This procedure is quite general.

Moulding powders filled with fabric shreds, etc., are very lumpy and uneven. They are not usually made into pellets or preforms.

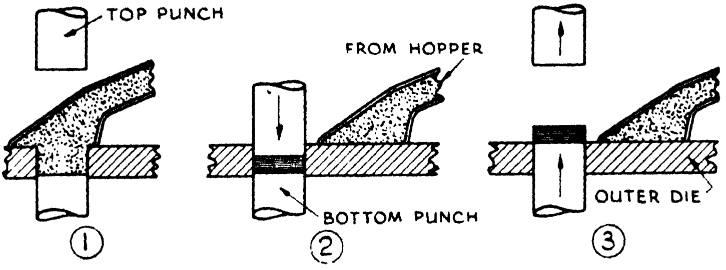


Fig. 62. Principle of operation of pelleting on preforming machine[7]

It is the general practice now to preheat moulding powder or pellets prior to moulding. This treatment shortens the time of cure and leads to smoother flow and characteristics and better mouldings. A preheat for about 20 minutes at 80° C. is fairly widely practised. The use of high-frequency methods for preheating pellets is gaining ground (*v.i.*).

Hydraulic Press. The press has been aptly described as the work-horse of the moulding industry. It is undoubtedly one of the fundamental machines in the plastics industry.

Presses are manufactured by firms which have specialised in the solution of the many engineering problems which are involved.

A press consists of a stationary *platen* and a movable platen, mounted in a suitable framework. Pressure is applied through the movable platen. In some types of press the movable part works upwards, and in others downwards. In either case the moving plate is attached to a ram through which the pressure is transmitted. The ram is activated by hydraulic pressure which may be developed by a pump associated with the press or alternatively transmitted from an accumulator. The accumulator itself is generally charged from a pump.

Small hand-operated presses are employed, usually for experimental work. With these it is possible to develop adequate pressure by means of a ram attached to a screw which is worked by a large hand-wheel. The disadvantage is that when the material flows the pressure is lost and must be followed up.

The type of press where the ram moves upwards has, of course, been in use in the rubber industry for many years. This is the plain upstroke press. The downward moving type of press has been developed specially for the handling of plastics. In the case of the typical rubber press the platens consist of steel chests which can be heated by steam or cooled by water. The heat developed by steam under pressure is transmitted to the material which is contained in the mould gripped between the platens. Suitable inlets and outlets for steam and water are features of such machines. The whole assembly is built into a convenient frame.

High hopes are held out for high-frequency electrical current as a heating medium, but this is still in its early stages (*v.i.*). In the normal way there is thermostatic control on such machines. The run of temperature normally employed may be up to 180° C., which is equivalent to a steam pressure of about 100 lb. per sq. inch. For moulding of phenol-formaldehyde resins, lower temperatures may be employed, e.g. down to 140° C., but in this case the time of setting will be correspondingly increased.

Fig. 63. A large press of 1,000 tons designed for very deep mouldings. Tables 52″ × 48″ with daylight of 60″ and stroke of 55″. The press weighs about 50 tons[5]

Heat transmission is one of the great problems in moulding. The limitations of moulding are entirely due to poor heat conductivity of the moulding powders. This limits the thickness of articles very severely.

The general type of moulding presses in use comprise the following:

Plain Upstroke, consisting of a hydraulic cylinder operating a ram which raises the bottom table. The fall of the ram is by its own weight under gravity. This is the cheapest form of press, but suffers from the

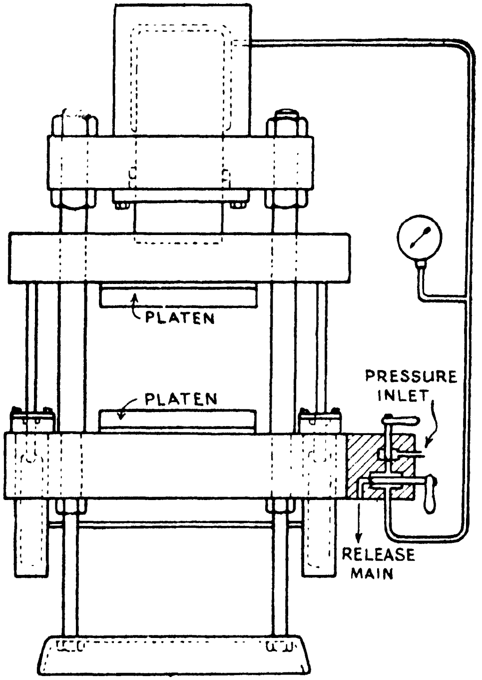


Fig. 64.
Downstroke press[7]

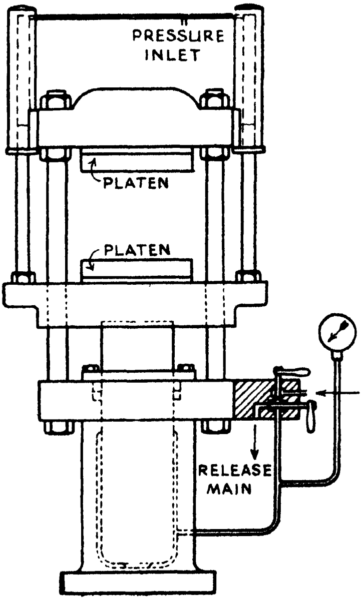


Fig. 65.
Plain Upstroke press with return rams[7]

disadvantage that it is slow in action and is liable to stick if the ram packing is too tight.

Plain Upstroke, with return rams. This arrangement overcomes the troubles due to tight packings, but slightly reduces the total tonnage of the press as the return rams take up some of the pressure.

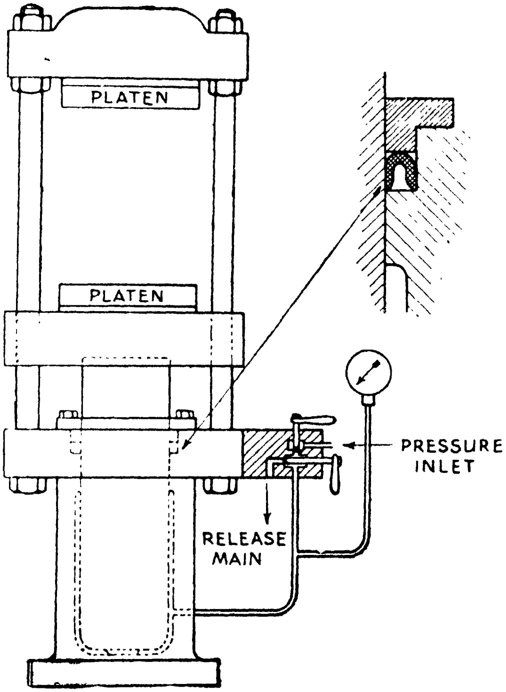


Fig. 66. Upstroke press—showing hydraulic system

Downstroke (sometimes called semi-automatic). As its name indicates, in this type of press the bottom table is fixed and the top table is connected to the hydraulic ram. These presses are always fitted with a return ram which pushes up the top table immediately the pressure is released from the main ram.

Downstroke with Pre-filler. This type of press is similar to the Downstroke Press, but with the difference that the main ram falls by gravity until pressure is needed, the space in the cylinder caused by the ram falling is filled from a pre-filler tank mounted on the head of the press and connected to it by means of a lightly loaded or hand-operated valve. When pressure fluid is admitted to the cylinder this valve is kept closed by the pressure. The return rams in this type of press cannot be of the constant pressure type, as the ram must fall by gravity, and to do this the return rams are connected by a hand-valve to exhaust by opening levers "a" and "b." The ram then falls by gravity, drawing in by suction hydraulic liquid from the pre-filler tank mounted on the press head. The valve "b" is then closed and the valve "c" is opened, which opens up the pressure supply, causing the ram to complete its stroke under full working pressure. The pre-filler valve is so counter-balanced that it returns to its seat and is held there by the pressure. When it is desired to open the press, valve "a" is closed (leaving the pressure supply to the return cylinders, but cutting off the supply to the main cylinder) and the pre-filler operating handle is pulled, allowing the return rams to push back the main ram to its top position and the hydraulic liquid to be returned to the pre-filled tank. The pre-filler type of press has the advantage of economy and speed of operation as hydraulic fluid under pressure is only called for during the final part of the stroke.

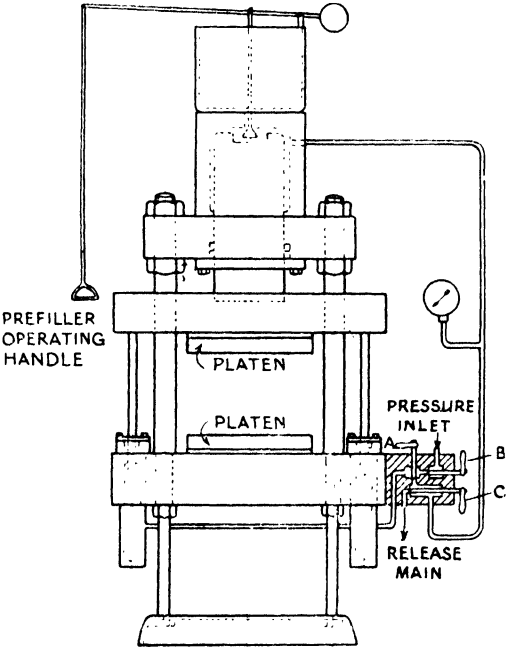


Fig. 67. Downstroke press with pre-filler[7]

Heating of Presses. So far as plastics are concerned, many presses have platens which are steam-heated and water-cooled. Other forms of heating, e.g. by electrical resistances, or by gas, are also used. The moulds, consisting of two or more parts, are placed between the platens and may be removed for filling and unloading.

In other types of presses the two parts of the mould are directly attached to the platens, one part to the bottom and one part to the top. In some cases the mould parts themselves may be cored for direct heating.

Steam. The platens are drilled through with a series of holes and cross-drilled and plugged to give a serpentine flow to the steam. Steam-heating is very convenient as it will provide easy temperature control, the temperature being directly proportional to the pressure. Thus, a steam pressure of 100 lb./sq. in. always corresponds with a temperature of 327° F. and 120 lb./sq. in. with 341° F. Thus a pressure gauge can be marked to read temperature directly. The temperature may be lowered by fitting a pressure-reducing valve before the steam inlet. (Size of boiler necessary can be approximately calculated by allowing 10 lb. of steam per sq. ft. for normal running, and twice this amount for warming up.)

Electricity. Either strip elements such as are used in a domestic electric iron, or long tubular elements pushed into holes drilled from the edge through the plates. The temperature of the platens is maintained within ± 5° F. by means of thermostats operated by a thermocouple also inserted into a drilled hole in the plates. The thermostat will switch off the current when the temperature rises too high, and switch it on again when too cool. The heated platens, while in good contact with the mould, must be efficiently insulated from the press itself, and for this reason a sheet of insulating material, such as mica, asbestos, or one of the many special compositions is put between them and the press.

Hot Water. Another school of thought favours the use of hot water instead of steam owing to the better thermal contact of water with the channels in the platen. For this, instead of tapping the steam from the top of the boiler, the hot water which is at the same temperature is taken from the bottom. The control of temperature to individual presses is not possible with the use of water.

Gas. This medium is successfully used in some plants, but suffers from the danger of fumes. The method used is to insert long burners into tunnels in the platen, and temperature control is by thermostat operating a control similar to the well-known "Regulo" as used for gas cookers.

The opening between the upper and lower platen is known as the *daylight*. The maximum daylight will depend on the length of stroke of the ram. For moulding plastics the press generally has a single daylight. For applications where high pressures for moulding will not be necessary, presses may have many daylights, there being a large number of intermediate platens which are brought together by the action of the ram. This type of press is widely used for moulding sheet and for lamination.

Pressure is usually developed hydraulically by means of water or oil. The liquid is either pressed against the ram by the direct action of a powerful pump—usually a three-throw pump—or by the direct pressure of an accumulator. The accumulator may be weight loaded, or loaded with water. It is itself operated by a pump. The advantage of using hydraulic pressure is that it is possible simply and smoothly to have complete control of whatever pressure may be needed up to the maximum available. The ram remains stationary when in action, and exerts a constant pressure on the mould.

Hydraulic Supply to moulding presses can be either through water or oil. Oil is expensive in first cost, but shows a considerable saving in maintenance costs, both on the presses and pumping equipment. It is rapidly replacing water as a hydraulic medium and makes for ease of control as easily operated piston-type valves can be used. These are not suitable for water: the screw-down type of valve must be used.

Pumps and accumulators. The action of a single-ram pump is extremely jerky and would cause too much vibration, and in practice it is usual for pumps to be fitted with a number of plungers driven by means of a crankshaft, which is arranged so that the delivery from one plunger commences at the end of the stroke of the others. In this manner smooth operation of the press is obtained, and there is little pulsation of pressure in the system. These pumps are usually driven by means of an electric motor.

The most common type of pump used for the operation of hydraulic presses is extremely simple in construction and incorporates two spring- or gravity-loaded non-return valves arranged so that when the plunger is withdrawn one of the valves opens and allows oil to be drawn by suction from a sump. On its return stroke the plunger compresses the oil (or water), closing the first valve against its seating and opening the second, which allows the oil to be forced into the pressure pipe-line.

Hydraulic presses do not require a constant supply of fluid during the period when pressure is being maintained. Because the presses are not drawing oil from the pump continuously, a smaller pump can be utilised if provision is made to store the operating fluid during the idle periods of the press. In this way it is possible to have available a supply of fluid for press operation which can be drawn upon at any time.

The tanks in which the fluid is stored are known as accumulators, and consist of a large tank which is capable of withstanding the operating pressure of the presses. The size of the tank is such that it will hold sufficient fluid to meet the demands of the press system more quickly than the pump can supply it. The capacity of the tank is varied by the movement of a ram on which is placed a dead weight the magnitude of which can readily be calculated from the line pressure required and the diameter of the ram in the accumulator. It is the ram and weight in the accumulator which control the pressure in the whole system.

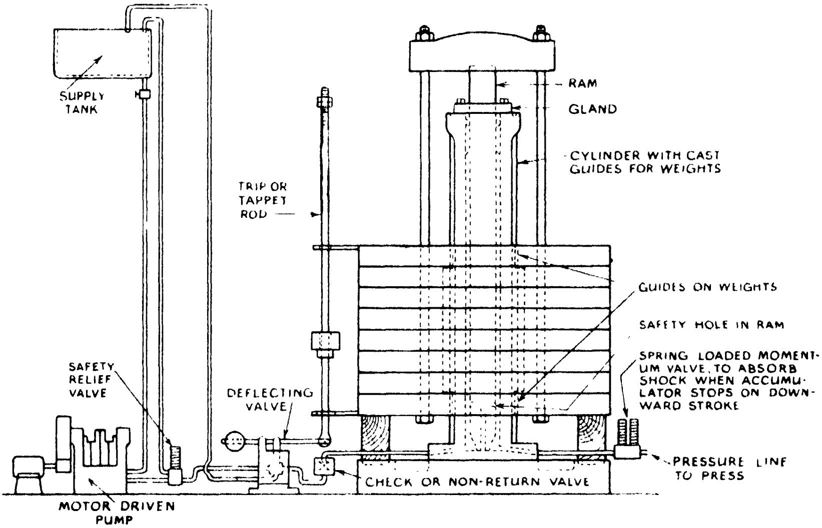


Fig. 68. Weight-loaded accumulator system from hydraulic supply to moulding press[7]

The choice of the hydraulic system to be used is made from the following:

(1) *Self-contained Units.* Each press is provided with its own individual pump. This can be mounted on the press itself or adjacent to the press. This system, while being of heavy first cost, is very flexible and enables a moulding shop to be expanded or the machines to be quickly

moved to other locations. Oil operation is usually employed in self-contained units.

(2) *Batch Operation.* This method of operation is popular as its cost and installed h.p. are lower than those of self-contained units. (Note: A self-contained unit needs a pump and motor of sufficient size for the maximum load demand of the press.) It is generally estimated that not more than 50 per cent of the presses will be operated at the same time. Care must be taken to fit non-return valves in the supply line to each press to prevent a fall in pressure on a press which has been closed, when another press is operated.

(3) *Accumulator Systems.* The hydraulic power is laid on in the same manner as an electric supply from a main generating station, and in order to balance the fluctuating demands for power an accumulator is necessary to keep a steady load on the pumps. The choice of the accumulator to be used lies between two main types.

(*a*) *Weight loaded.* This consists of a hydraulic ram fitted into a cylinder mounted vertically. The ram is loaded by cast-iron weights or, alternatively, with scrap iron in a tank attached to the ram and exerting a pressure of 1 or 1½ tons per sq. in., depending on the pressure chosen for the system. The size of the accumulator is calculated and the frequency with which it will be opened and closed. The ram operates a deflecting valve when at its full height to cut off the supply of fluid from the pump and prevent accidents. The pump used to supply the accumulator is generally of the conventional treble barrel vertical type, motor-driven.

In some plants using a number of Upstroking Presses, in which a lower pressure can be used to close the press during the major part of its stroke, a low-pressure hydraulic system is laid on in addition to the high pressure; this is generally worked on a pressure of 300–500 lb., as it is less costly to pump water at this pressure than at 1 to 1½ tons. An additional low-pressure accumulator and pump is installed.

(*b*) *Air-loaded.* This system (Fig. 69) uses the principle of compressing air or gas which acts as a spring above the liquid and maintains the pressure when the liquid is taken from the container. The container is first of all filled with compressed air at some pressure below that of the hydraulic system, and then the liquid is pumped into the container, which further compresses the air until sufficient liquid has been pumped in to obtain a balance of pressure. A typical example would be for a hydraulic system working at 2,000 lb. per sq. in. with a 1,000-cu. ft. air accumulator. The accumulator would be charged with air at 1,500 lb. per sq. in. When the hydraulic pump is started up water will be pumped into the container at 2,000 lb. per sq. in., and when 250 cu. ft.

of water has entered, the pressure of the whole accumulator will rise to 2,000 lb. This is because the air pressure follows the law:

$$
\begin{array}{rcll}
\text{Pressure} & \times & \text{Volume} & = \text{Constant.} \\
\text{i.e. } P_1 & \times & V_1 & = K \\
1{,}500 & \times & 1{,}000 & = 1{,}500{,}000 \\
P_2 & \times & V_2 & = K \\
2{,}000 & \times & V_2 & = 1{,}500{,}000 \\
\multicolumn{4}{l}{\text{therefore } V_2 = \dfrac{1{,}500{,}000}{2{,}000} = 750 \text{ cu. ft.}}
\end{array}
$$

The air accumulator has the big advantage that there are no moving parts, and consequently no leakage. There are no packings to be maintained, but there is the disadvantage that whenever water is taken from the accumulator there is a small drop in pressure owing to the operation of the PV = K law. Thus, if a press is operated needing, say, 20 cu. ft. of water, the pressure will then be reduced to

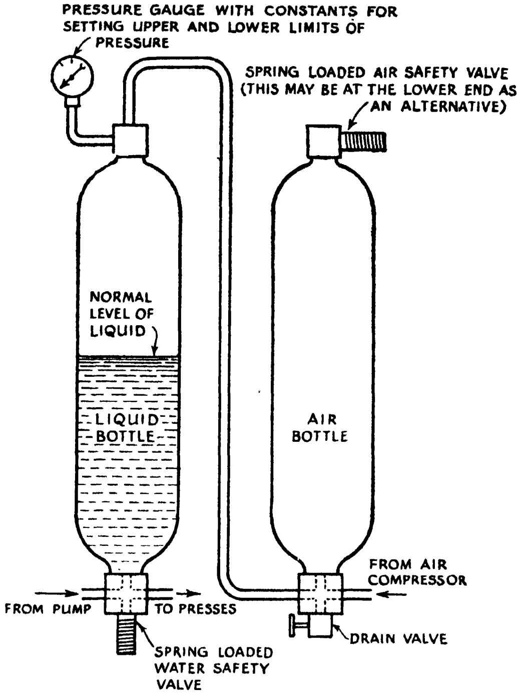


Fig. 69. Air-loaded accumulator system[7]

$$\frac{750}{750} \times 2{,}000 = 1{,}950 \text{ lb. approx.}$$

The pressure drop can be reduced by the use of larger accumulators. For instance, in the example given above, if the accumulator had been of 2,000 cu. ft. capacity instead of 1,000, the pressure drop would have been only 25 lb. Another limiting factor is the initial air pressure, which determines the amount of pressure fluid which the accumulator will take. In the example chosen, we have assumed an initial pressure of 1,500 lb. per sq. in., but had this been 1,000 lb., 500 cu. ft. of water would have been pumped in and the pressure would have dropped to 1,900 lb. per sq. in., when 20 cu. ft. of water was drawn off.

Fig. 70. A typical British moulding plant

A 100-ton press gives 100 tons pressure on the platens. If, therefore, moulding is to be carried out at 1 ton per sq. in., then the effective area of the moulding, or mouldings, must not be greater than 100 sq. inches. Thus the press could handle one moulding of 100 sq. inches effective moulding area, or 10 mouldings each with 10 sq. inches effective moulding area, or 100 mouldings with 1 sq. inch effective moulding area.

In the case of a press where the ram works upwards, i.e. the lower table moves, the mould may be independent of the press. It can be a hand-mould or fitted to the machine. With a downstroke machine the mould must clearly be a part of the machine so that the two parts must be fixed.

Methods of Moulding. Compression moulding of phenolic resins is accomplished by three methods: (1) They may be handled *manually* in straightforward moulds, which are placed between the heated platens of a hydraulic or suitable mechanical press, being removed by hand when the moulding operation is finished. The moulding is then extracted. This follows rubber practice. (2) *Semi-automatically*, where the moulds are fastened to the platens of the press and the parts are ejected from the mould as the press opens; and (3) the moulding may be *fully automatic* where the processes of weighing or measuring, charging the mould, closing it, opening, ejecting and removing the pieces from the mould are carried out by suitable mechanical and electrical means.

TABLE 52

COMPRESSION MOULDING TEMPERATURES

Typical Standard Materials	Normal Compression Moulding Temperature Range deg. C.
1. Phenol-formaldehyde (wood flour) . . .	140–180
2. Urea-alpha cellulose filler	135–160
3. Melamine-formaldehyde	140–175
4. Cellulose acetate	135–150
5. Methyl methacrylate moulding powder . .	140–180
6. Polystyrene	120–180
7. Polyvinyl chloride-acetate	120–170

The economy and suitability of the method used depends upon the design of the part, the total quantity and the rate of production desired.

For the general type of phenolic moulding powder with wood flour as filler, the moulding temperature may vary from 140° C. up to 180° C., depending on the material used and the design of the article to be made.

A short time after the hydraulic pressure has been applied the mould is opened and the moulding is removed, a faithful reproduction of the mould. In the normal way a full cure is required. Phenolic resins are not particularly sensitive to overcure unless the temperature is very high, i.e. greater than 180° C., when blisters are formed, followed by charring if the heating is continued. If the article is under-cured the moulding may be cheesy. Where powder has not flowed adequately there may be rough patches or it may be distorted when ejected or removed.

Usually the moulding is automatically pushed out of the mould by means of ejector pins which are brought into action at the end of the moulding cycle.

Angle Press. The tendency is to make more and more complicated mouldings. Where undercuts and complex designs are involved, it is often impossible to manage with a two-piece mould. Split moulds are essential. In such cases there must be horizontal pressure applied in order to hold the various parts of the mould together. The angle press is designed to handle such mouldings. A vertical ram operates downwards in the normal manner. In addition there is a horizontal ram to hold the split mould parts in position. In ordinary practice the horizontal ram develops higher pressure than the vertical ram, otherwise it would be forced open during moulding operations.

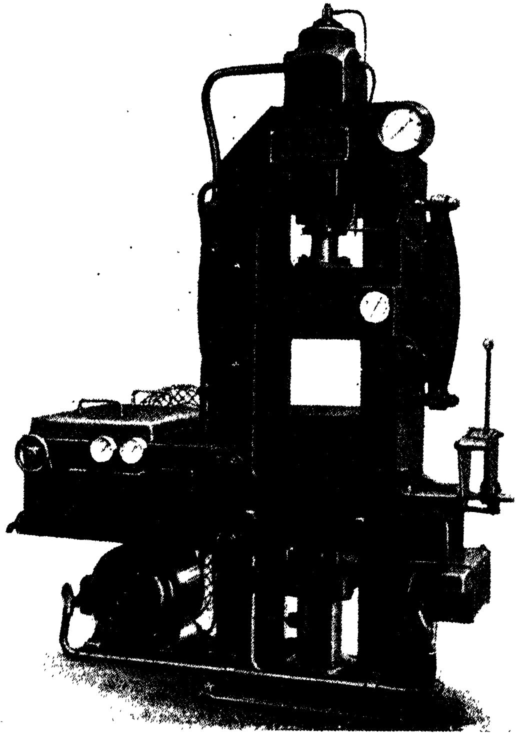


Fig. 71. 25-ton self-contained unit of press and pump[6]

The mould is first assembled and held by the horizontal ram. The preforms or powder are put in, and the ordinary curing cycle carried through, i.e. the vertical ram descends, heat and pressure coming into play. After moulding, the vertical part of the mould is first removed, followed by opening up horizontally. The moulded article is then removed and finished off.

Moulding Time. The time taken for moulding will vary according to the type of phenolic moulding powder employed. It will also depend upon the article to be moulded, its dimensions, any inserts, and particularly thickness. The time will obviously depend upon the temperature and pressure employed at the present time. A small thin-walled article may be moulded well within a minute. For example, a bottle-cap requires less than a minute to mould. It has been found that with increasing thickness the time required is more than the proportional increase in thickness. By way of example, with an average article of the thickness of 0·125 inch the cure may take up to 3 minutes. A radio cabinet, for example, requires about 8 minutes for completion. The use of high frequency pre-heating has greatly speeded up production particularly of thick articles. In the case of phenolic moulding powders the finished moulding is ejected while hot. This is evidently a great advantage and enables very speedy production. The fundamental requirement is to heat long enough for the heat to penetrate right through the material. To cure an article ½ inch thick may take 20 minutes, while a 2-inch section may require something like 1¼ hours. In these instances nearly always the centre is undercured while the outside tends to be overcured.

When an article has been ejected the mould is freed from any residual particles of powder that may lurk in the corners by means of a powerful jet of compressed air at 100 lb. per sq. inch pressure.

Moulds. The production of moulds is a very intricate form of engineering involving the use of the most modern engineering equipment. Apart from the design of individual moulds, it is necessary to be able to reproduce as many moulds as may be necessary. The moulds should be designed to cope with the mass of repetition work involved in large-scale production.

Where large numbers of comparatively simple moulds are being made, the process of hobbing is employed. This involves pressing a hard steel master-die into a much softer steel hob. The reproductions of the mould obtained in this way are then hardened. Obviously a large number of such apertures can be made in a single slab of metal, and is suitable for the large-scale moulding of various articles.

Usually the moulds are prepared from specially hardened steel. This is necessary in order to stand up to the high hydraulic pressures which are employed. They are very often chromium-plated. This serves a dual purpose, inasmuch as it helps to resist the corrosive influence of phenolic derivatives at high temperature, and it also gives a superb polish. In any event moulds are always highly polished. Their design and production is a highly skilled form of engineering, being one of the specialised branches of the industry. It is evident that such moulds must of necessity be expensive, and their cost can only be justified by the production of many thousands of mouldings from a single mould.

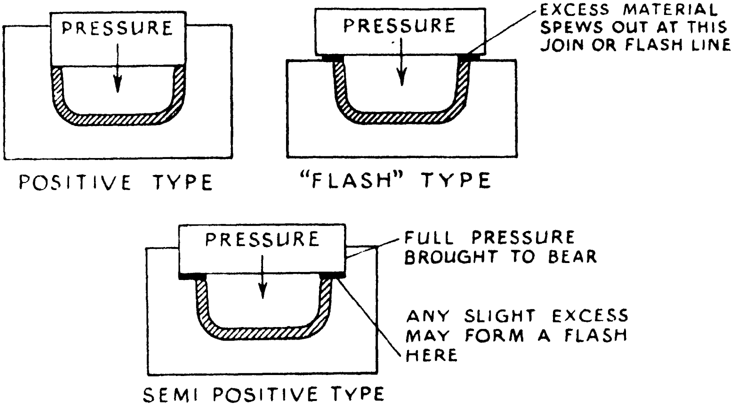


Fig. 72. Types of moulds

Much progress has been made in recent years in the process of compression moulding. The number of cavities in a single mould has increased from a maximum of 40 in 1925, until at the present time, for small moulded parts, 200 cavities are commonplace.

The salient features in the construction of moulds have been outlined by Young.[3] He suggested that mould design can be affected by:

(*a*) Materials to be moulded and their characteristics.
(*b*) Pressures and frictions set up in the mould.
(*c*) Materials for mould construction.
(*d*) Thermal conditions in the mould and adjacent to the mould.
(*e*) Methods of operating and maintaining the mould.

So far as the actual choice of metals was concerned the factors to be considered were:

1. Differences in coefficients of expansion.
2. Ease of freeing the moulding from the metal surface.
3. Difference in friction between parts that have relative movement.
4. Ease of extrusion where the moulded material moves across the face of the metals.

5. Hardness of the metals to stand up to the cracking and opening of the moulds and insertion of metal parts.

The aspects of the behaviour of the material, e.g. phenol-formaldehyde moulding power which had influence on the mould be described as:

1. Temperature at which the material is plastic, and the time it takes to reach this plastic condition.
2. The pressure set up by material when first introduced to the mould, before it becomes plastic.
3. The resistance to flow at the initial stage of moulding.
4. The resistance to flow when the material is plastic.
5. The resistance to flow at the latter end of the plastic life of the material.
6. The abrasive action of the material on the mould surface.
7. The coefficient of expansion of the material itself.
8. Any tendency to set up a rapid chemical action.
9. The bonding tendency of the material to the mould face.
10. The shrinkage of the material.
11. Effect of mould lubrication on the material being moulded.

Types of Moulds Employed. In principle, there are two primary types of moulds used in pressing phenolic powders. They are known respectively as "*Flash*" moulds and "*Positive*" moulds.

The "flash" type of mould, which is also known as the "overflow" mould, is made so that the upper and lower portions rest one on the other as they are brought together under pressure. Alignment is secured by the use of dowel pins. The material may be either powder, if the mould is sufficiently deep compared with the size of the piece to be moulded, or pellets or a suitable preform tablet. There must be a slight excess of moulding material available over and above the actual amount necessary for the moulding. This excess material is squeezed out at the join as the edges of the mould come together, and is known as the "flash." There is a tendency for the pressure to diminish as the edges of the mould are reached, so that the moulding tends to become weaker towards the periphery.

In the "positive" mould the upper part of the mould or the top force or plunger telescopes into the lower portion of the mould. As there is no outlet for excess material or "flash" in this case, an exact quantity of the moulding material is essential. Consequently the moulds must be made sufficiently deep to hold the complete charge of powder. It is employed for deep-drawn mouldings. Powder is usually employed in this type of mould. The full possible pressure is brought to bear, giving a firm dense moulding.

As a matter of interest the usual type of phenolic moulding powder, based on wood flour as filler, compresses to about 40 per cent of its initial volume.

In actual practice, the most widely used type of mould is a compromise between these two types, and is known as the "*semi-positive*" mould. It is the most versatile form of mould. The lower part of the mould is deeper than in the case of the flash type, so that powder may be freely employed. The top part of the mould fits completely into the lower part after the fashion of a "positive" mould, and the full pressure is finally taken up inside the mould for a short distance at the end of the stroke. As a result the full mould pressure is attained at the end of the stroke, giving the same densifying effect which is produced by positive moulding. As a result, rather better mouldings are obtained than with the "flash" type where the pressure exerted falls away towards the edges. This is particularly the case where very "deep draw" products are being made.

Moulding Faults. Redfarn[1] has admirably summarised the chief faults which may occur in moulding phenolic wood flour filled material.

(1) Precuring, which shows up on the underside of the moulding as a slight chalkiness, in which the outlines of individual moulding powder particles can be seen. Precuring is caused by the powder coming in contact with the hot mould surface before the moulding pressure has been applied. The fault can be overcome by a quicker closing of the mould or by working at a lower mould temperature.

(2) Flabby, blistered mouldings, difficult to eject, but which will, however, set hard on cooling usually with some distortion, are obtained if the moulding time for the particular temperature used has been too short. Raising the temperature or increasing the moulding time will overcome this fault. Hard, blistered mouldings may sometimes be obtained if the moulding time is very considerably prolonged.

(3) Short mouldings occur when too little moulding powder has been put in the mould cavity or too stiff a moulding powder has been used. The obvious remedies are to increase the charge or to use a softer powder.

(4) Streaky mouldings are sometimes obtained when a cold powder is put into a mould having a large surface area over which the powder has a fair distance to travel. The powder immediately in contact with hot mould surface becomes partially cured before the pressure is applied, and when pressure is applied the partially cured powder has thus a different degree of flow from the cold powder above it. Two particles

of powder of different flow moulded side by side will give rise to streak marks. The trouble can be overcome by preheating the powder and lowering the mould temperature with corresponding lengthening of moulding time.

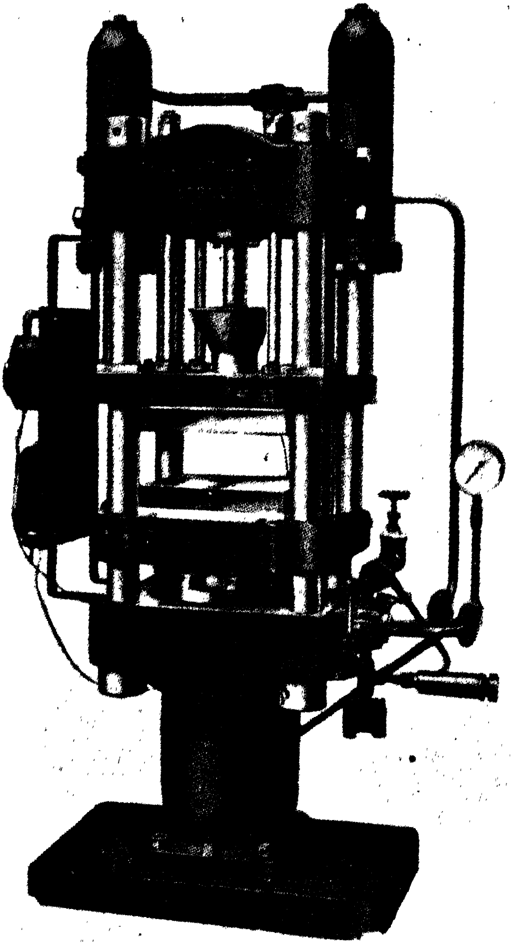


Fig. 73. Fifty-ton press for transfer moulding[7]

(5) Core is the name given to a cokey centre in a thick moulding. If the cokey centre contains a cavity it is called a void. Both of these defects are brought about by the poor thermal conductivity of the moulding powder, which allows the outside surface of the moulding to

cure and set before the inside of the moulding has become hot enough to flux under pressure. Cores and voids can be avoided by preheating the powder and lowering the mould temperature with corresponding lengthening of the moulding time.

(6) Underloading of the mould gives a characteristic moulding with a crumbly edge, caused by lack of pressure. Increasing the charge in the mould cavity overcomes this trouble.

(7) Overloading the mould, indicated by an excessive amount of spew during moulding, gives a moulding with an unduly thick flash, and hence of the wrong dimensions. Reducing the charge overcomes this trouble.

(8) Occasionally a moulding will stick in the mould and is difficult to eject. Undercuring or the use of too high a temperature are often the causes.

(9) Cracking round metal inserts when a moulding cools occurs sometimes because the moulding composition has a greater contractability than the metal. The stresses can be relieved and the cracking prevented by wrapping the insert with cotton, silk, or woollen tape before moulding.

Transfer Moulding of Phenolic Moulding Powders. A method of moulding which has achieved great importance during recent years is known as *transfer moulding*. The preformed material is placed into a heated chamber. It is subjected to heat for a short time, and is then forced through an orifice into the mould by a plunger working at high pressure. The mould is heated up to the full setting temperature required. The moulding rapidly sets, and is then either ejected or removed by hand.

The material in the chamber is heated up to a temperature of about 80° C., so that it is just beginning to become plastic. The piston or plunger descends on this at a pressure of the order of 12 tons per sq. inch. The intense friction developed at the orifice raises the temperature to such an extent as to make the moulding powder almost fluid, so that it flows readily into the mould. It is essential that the plunger should be a very good fit into this container.

The advantages of the process are many. It enables the moulding of deep-drawn and intricate patterns to be carried out successfully. One of the great difficulties in compression moulding is the distortion and displacing of inserts. High local pressures caused by hardened sections of resin readily push pins out of shape.

Transfer moulding does not have this effect, and the most delicate inserts can confidently be moulded in without any troubles. The procedure has proved advantageous in the use of materials which are difficult to mould such as fabric-filled powder or mineral-filled powders, etc.

The relatively poor flow characteristics of these materials do present real difficulties in ordinary compression moulding. They prove very amenable when moulded by this injection process. Particularly in the case of mineral fillers, however, the wear on the orifice or nozzles is excessive, and care has to be taken in this respect.

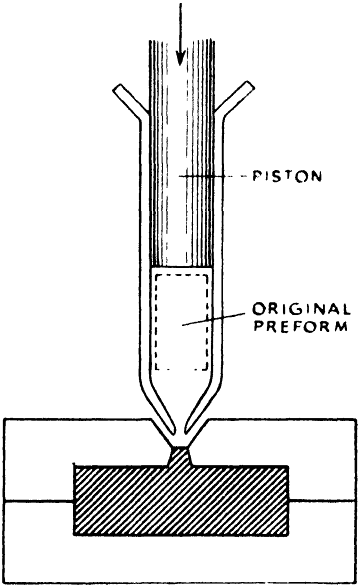


Fig. 74. Transfer moulding

A further development in this field is the so-called jet moulding process, pioneered by Shaw.[2] While the conditions are in many respects similar to transfer moulding, a cooling procedure is introduced around the nozzle, so that there is no tendency for setting of the resin here. The material retains its thermoplastic characteristics, and, as a consequence, continuous injection moulding can be carried out.

REFERENCES

1 Redfarn. *British Plastics*, 1943, **15**, 235
2 Shaw. U.S.P. 2,296,295/1942.
3 Young. *Rubber Age*, 1943, **23**, 108.
4 Photographs by courtesy of Bakelite, Ltd.
5 ,, ,, Hydraulic Engineering Co., Ltd.
6 ,, ,, I.C.I. (Plastics) Ltd.
7 ,, ,, Alfred Herbert Ltd.

CHAPTER VIII

UREA-FORMALDEHYDE RESINS

UNTIL comparatively recent years phenolic resins had a number of important limitations. In particular, really satisfactory light-coloured products could not be obtained. Consequently there was always some pressure to find synthetic resins which would give mouldings in a better range of colours. It had been found that urea and formaldehyde combined to form glass-like resins. These are referred to as urea-formaldehyde resins, urea resins, or as aminoresins. The transparency of these resins in the first place suggested the possibility of making organic glass. Apart from this angle, which was actively pursued, although without success, it did show clearly the practicability of making gaily-coloured articles in transparent and translucent colours and pastel shades, and so on.

The fact that phenolic resins could not be moulded into satisfactorily coloured articles tended to limit their scope to utilitarian products. In addition there was always the hangover of the odour of phenol or cresol. In other fields of applications it was also sought to have rather better electrical characteristics than were available with phenolic resins. This particularly applied to the resistance to electrical tracking.

While these objections have been virtually eliminated yet they supplied a driving force for the development of other resins, notably the urea-formaldehyde type. Urea-formaldehyde resins are definitely thermosetting. When heated they first become thermoplastic and then set to an infusible mass. Over 24,000 tons urea moulding powders were used in the United States in 1947.

Another practical aspect of great importance was the fact that moulding conditions for phenolic resins, particularly the high temperatures used, were very exacting, and materials which could be handled at lower temperatures held attractions. The outstanding features of aminoresins are the colour possibilities, the ability to retain these colours under conditions of heat, or exposure to light. They also give excellent adhesives.

Although the colour angle was the first main factor in the development of urea resins, the most important factor at the present time is the binding power. The use of urea resins for low temperature setting adhesives for plywood, laminates and so on, is of major industrial importance.

Synthetic resins have been made for many years by combining urea, or related materials, such as thiourea, or guanidine, with formaldehyde or other aldehydes. They have been made for a variety of purposes in a number of different forms. For example, water-soluble resins have been widely used for making plastic adhesives for treatment of textiles, and so on. Resins soluble in organic solvents have found their greatest utility as coatings. The latter application has acquired great significance, and the term urea resins is applied widely not only for straight urea-formaldehyde types, but also to products where these resins have been modified by the inclusion of alkyd resins, and so on.

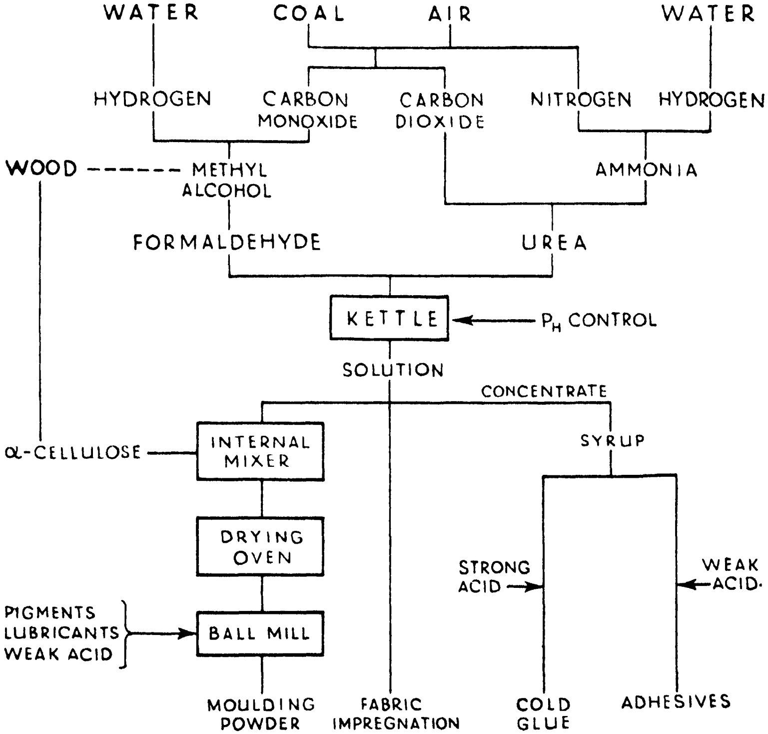


Fig. 75. Flow sheet for urea-formaldehyde resins

Urea resins are indeed truly synthetic. While commercial production starts from urea and formaldehyde, these chemicals in turn are made synthetically from four gases—urea from ammonia and carbon dioxide, and formaldehyde from hydrogen and carbon monoxide.

Other materials resembling urea also form synthetic resins—notably thiourea which is widely used, and guanidines.

Urea resins can be divided into two groups:

1. The so-called "straight" types which are solutions of urea-formaldehyde resins alone. These are practically colourless, and yield films which are very hard but relatively brittle. They were the first reaction products of urea and formaldehyde to attain practical importance. They were prepared in water solution and found extensive use as adhesives, textile finishes, moulding powders, laminating solutions, etc. However, these aqueous types are insoluble in nearly all the common organic solvents. They are incompatible with alkyd resins varnishes, and lacquers.

2. The difficulties were overcome by the preparation of urea-resins containing alcoholic ingredients. These "modified" resins are predominantly urea types in composition and characteristics. They have been modified by inclusion of alkyd resins or other materials to alter distensibility, adhesion, and other characteristics. The extent to which such resins retain the characteristics of straight urea types depends, of course, on the kind and proportion of modifying material.

The Properties of Urea. The most important method for making urea is by the interaction of carbon dioxide and ammonia. Such production is generally associated with nitrogen fixation plants.

Until 1935 Germany was the sole producer of synthetic urea. Early in that year in England, Imperial Chemical Industries, Ltd., commenced production of synthetic urea. Later in the same year commercial production of synthetic urea began in the United States. In 1936 it was estimated that world production of synthetic urea was about 150 tons per day. Present U.S. production is about 50,000,000 lb. per annum, all of which goes into plastics.

In effect the process consists of subjecting ammonia, carbon dioxide, and water, to high temperature and pressure. The process can be made continuous. Ammonium carbamate appears to be formed as an intermediate product. The production is accompanied by acute corrosion difficulties. While ammonia, carbon dioxide, and water by themselves are practically harmless to steel, yet when combined they are extremely corrosive.

Pure urea is a white odourless crystalline solid m.p. 132°C. which is freely soluble in water.

Thiourea is a white crystalline material m.p. 170°C. It is widely used in moulding powders together with urea. It improves water resistance.

Background of Urea-Formaldehyde Resins. Holzer[10] in 1894 obtained white insoluble precipitates from urea and formaldehyde in the presence of dilute acids. This was considered to be methylene urea.

This reaction of formaldehyde with urea was studied by Goldschmidt[6] in 1896 who condensed them in a neutral solution and also in an acid solution, obtaining white granular resins.

The first systematic investigation of the reaction was carried out by Einhorn and Hamburger[5] in 1908. They isolated dimethylol urea, a crystalline soluble material melting at 120° C. At 137° C. it formed an amorphous substance.

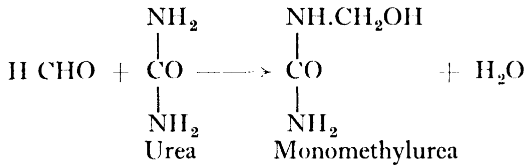
John[12] in 1920 was the first to realise the potential importance of the resins, particularly as surface-coating materials. He prepared an adhesive by treating urea with an excess of formaldehdye. He actually heated one part of urea with five parts of formalin and removed half the liquid by distillation. The resulting material could be hardened by heating at 80° C. Goldsmith and Neuss[7] added definite quantities of acids up to ½ per cent of the urea during condensation. They found that addition of acid-condensing agents reduced the proportion of formaldehyde necessary for the reaction. Mittasch and Raustetter[14] in 1921 proposed the use of mineral acids and acid salts as condensing agents. They also suggested the use of organic salts. They followed this up by the discovery that rigid control of the acidity resulted in improved products. So they proposed the use of buffer mixtures such as citric acid and sodium citric and acetic acid and sodium acetate to keep the pH value constant. One example was to make a concentrated solution containing 6 parts of urea, 0·11 parts mono sodium phosphate, and 0·04 parts disodium phosphate. This was added to 25 parts of boiling 30 per cent formaldehyde. It was evaporated in vacuum below 50° C. to form a syrup which contained 15 per cent water. The result was a stable material which could be cast and if heated at 65° C. for two days gave a clear, transparent product.

Pollak[14] in 1921 used an alkaline condensing agent such as ammonia pyridine or hexamethylenetetramine. For example, one mol urea with three mols formaldehyde could be evaporated to a syrup at 75° C. to give a fusible insoluble resin. Pollak brought out the first commercial urea moulding powders known as "Pollopas" in 1923.

According to Hodgkin and Hovey,[9] the outstanding obstacle against the use of urea-formaldehyde resins for surface coatings is the lack of stability. After standing for the short period of two weeks, most urea-formaldehyde resins solutions give white precipitates or gels. In moulding compositions this is not so important nor so evident since it does not unduly affect the flow conditions at high temperatures.

Chemistry of Urea Resins. The following is a summary of the chemistry of the urea-formaldehyde resins formed in aqueous medium,

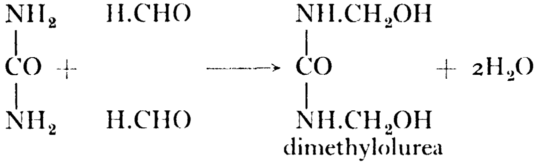
(1) One mol urea and one mol formaldehyde in the presence of hydroxyl ions form monomethylol urea (Einhorn and Hamberger).



$$\mathrm{H\,CHO} + \begin{array}{c}\mathrm{NH_2}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{NH_2}\end{array} \longrightarrow \begin{array}{c}\mathrm{NH.CH_2OH}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{NH_2}\end{array} + \mathrm{H_2O}$$

Urea Monomethylurea

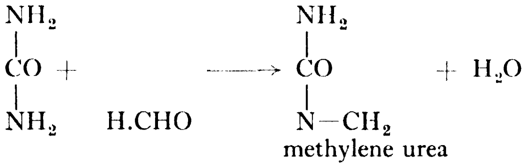
(2) When excess formaldehyde is present, e.g. 1 mol urea and two mols formaldehyde, then dimethylol-urea is formed.



$$\begin{array}{c}\mathrm{NH_2}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{NH_2}\end{array} + \begin{array}{c}\mathrm{H.CHO}\\ \\ \\ \\ \mathrm{H.CHO}\end{array} \longrightarrow \begin{array}{c}\mathrm{NH.CH_2OH}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{NH.CH_2OH}\end{array} + 2\mathrm{H_2O}$$

dimethylolurea

(3) When dilute acid is present then methylene urea is formed (Holzer).



$$\begin{array}{c}\mathrm{NH_2}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{NH_2}\end{array} + \mathrm{H.CHO} \longrightarrow \begin{array}{c}\mathrm{NH_2}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{N{-}CH_2}\end{array} + \mathrm{H_2O}$$

methylene urea

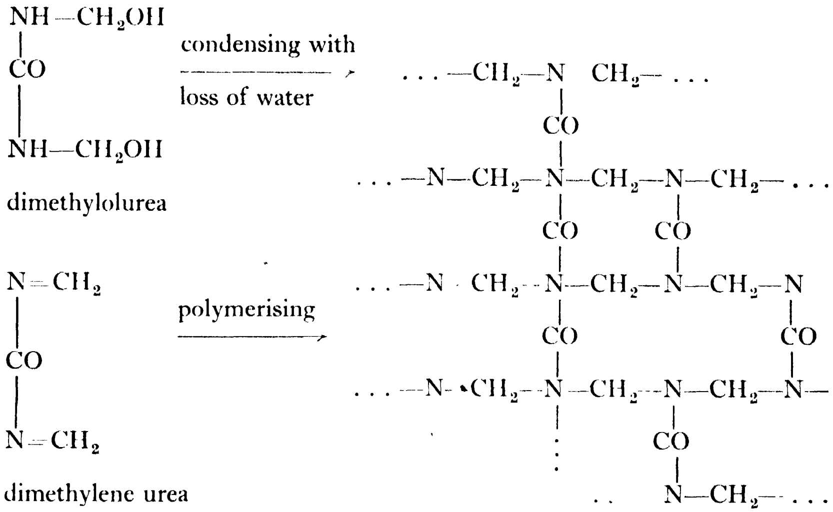
These reactions are fairly well defined and there is no controversy about them. But as to what happens thereafter, there is no fully accepted explanation as yet.

The facts are that gelation occurs and a thermosetting action takes place. According to accepted ideas their behaviour is invariably associated with the growth of a three-dimensional structure. Apart from this there is very little positive evidence about the structure of urea resins.

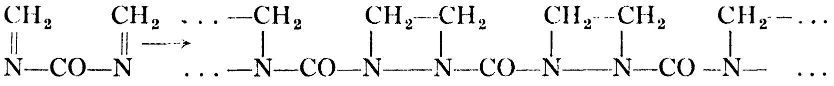
According to Hodgkin and Hovey there are two possible mechanisms for the formation of this three-dimension structure with excess of formaldehyde present:

(*a*) *Condensation* through dimethylolurea proposed by Walter and Gewing.[21]

(*b*) *Polymerisation* through dimethylene urea proposed by Scheibler[19] and Redfarn[16] respectively.



Dimethylene urea does not appear to have been prepared. Redfarn[17] who has been active in this field, at one time favoured the possibility of a straight linear chain being formed by polymerisation of dimethylene urea. Although an attractive possibility such a chain would not account for the setting characteristics.



$$\begin{array}{ccc} \mathrm{CH_2} & & \mathrm{CH_2} \\ \| & & \| \\ \mathrm{N} & \mathrm{-CO-} & \mathrm{N} \end{array} \longrightarrow \begin{array}{cccccccccccc} \ldots\mathrm{-CH_2} & & \mathrm{CH_2} & - & \mathrm{CH_2} & & \mathrm{CH_2} & - & \mathrm{CH_2} & & \mathrm{CH_2} & -\ldots \\ | & & | & & | & & | & & | & & | & \\ \ldots\mathrm{-N} & \mathrm{-CO-} & \mathrm{N} & - & \mathrm{N} & \mathrm{-CO-} & \mathrm{N} & - & \mathrm{N} & \mathrm{-CO-} & \mathrm{N} & -\ldots \end{array}$$

From either the methylol urea or the methylene urea compound the resulting condensation product is dependent upon the following conditions:

(*a*) The catalyst employed and the pH of the solution;
(*b*) The molecular ratio of the reacting components, and
(*c*) The time and temperature of the reaction.

The setting behaviour of these resins may be profoundly molified by suitable conditions. Salts of weak acids, having an alkaline reaction tend to halt the reaction. On the other hand, salts of strong acids, such as nitrates, sulphates and chlorides, accelerate it. By use of such materials it is possible to hasten the setting profoundly, as in the case of rapid-setting cements.

The Preparation of Urea-Formaldehyde Resins. The actual urea-formaldehyde resin is not prepared and isolated as in the case of phenol-formaldehyde resins. The resins are prepared either as aqueous dispersions or as solutions in other media or as moulding powders. The latter is the most widely known form.

Urea-formaldehyde moulding powders are prepared in two steps. One molecule of urea to two molecules formaldehyde are the theoretical proportions required to make a thermosetting material. In order to avoid moulding difficulties usually 1·5 to 1·6 molecules of formaldehyde are used. There is little effect on the setting behaviour. If more formaldehyde is present there are two disadvantages:

(*a*) Gases are given off during subsequent moulding, tending to form blisters, etc.

(*b*) The water absorption of mouldings, etc., is higher.

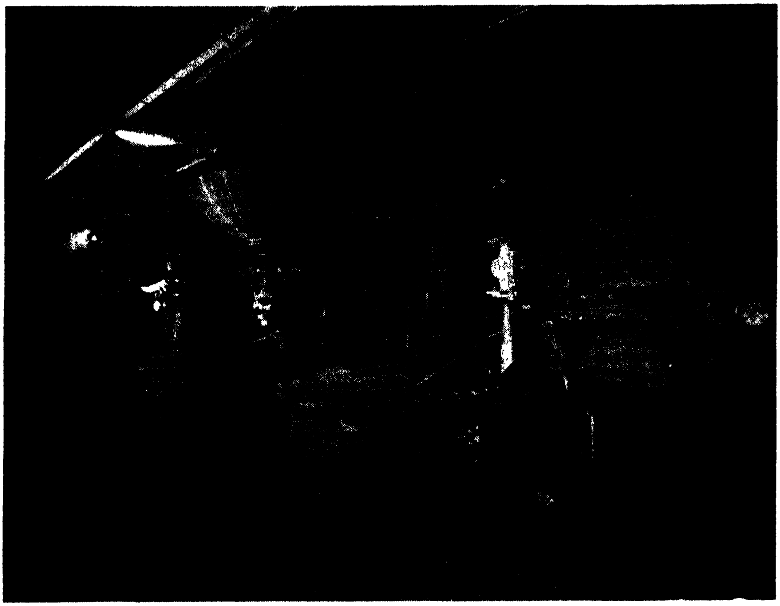


Fig. 76. A unit for manufacturing urea-formaldehyde syrups[23]

The First Stage. Neutralised formalin, urea and a small amount of ammonia are allowed to stand in the cold for about two hours. After this time a transparent solution is obtained containing 60 per cent resin. The liquor is mixed with about one-third of its weight of cellulose, which acts as a filler. The cellulose is used normally either as pure alpha-cellulose, as cotton linters, as wood pulp, or as wood flour. The filler is mixed with the solution at about 50° C. in an internal mixer.

A damp, pulpy mixture is obtained, which is spread in trays. These are dried below 90° C. At this stage a small amount of zinc stearate, the requisite colouring material, and 1 per cent of a solid acid is added to the mixture which is then ground in a ball mill. Zinc stearate is intended to act as a mould lubricant; the solid acid acts as a hardening catalyst.

The Second Stage. This stage of the process occurs under the influence of heat during the moulding process. The acid catalyst reacts with the urea-formaldehyde resins and accelerates its conversion to the hardened insoluble condition.

Significance of Cellulose as Filler. In the case of aminoplastics, much paper filler is employed in preference to wood flour. It is used in the form of pulp or alpha-cellulose sheet, being impregnated with the aminoresin as an aqueous syrup. The process is operated hot, the syrup being introduced under vacuum and forced to penetrate the filler by applying a pressure of 5 to 10 atmospheres. The dried material is then ground, after which pigments, etc., are incorporated as already described.

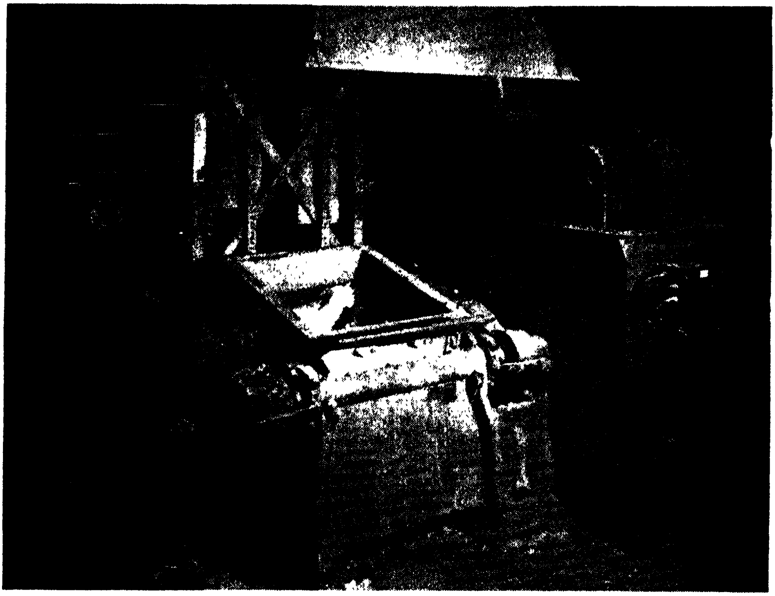


Fig. 77. Mixing urea-formaldehyde syrup and paper for moulding powder base[23]

The preference for cellulose in the form of cotton or paper for these resins rather than using the cheaper and rather less-pure wood flour, is accounted for by the fact that in some obscure manner combination occurs between urea resins and cellulose. As a result, the product is translucent, and wherever this property is required paper filling is advantageous. In this respect, the behaviour is in sharp contrast to that occurring with phenolic resins. The translucency is aided by the vacuum-pressure impregnation process. Small quantities of mineral fillers may be added during the impregnation process in order to form the basis for the preparation of moulding powders in light pastel shades. Fillers used include the white pigments, such as lithopone or titanium oxide.

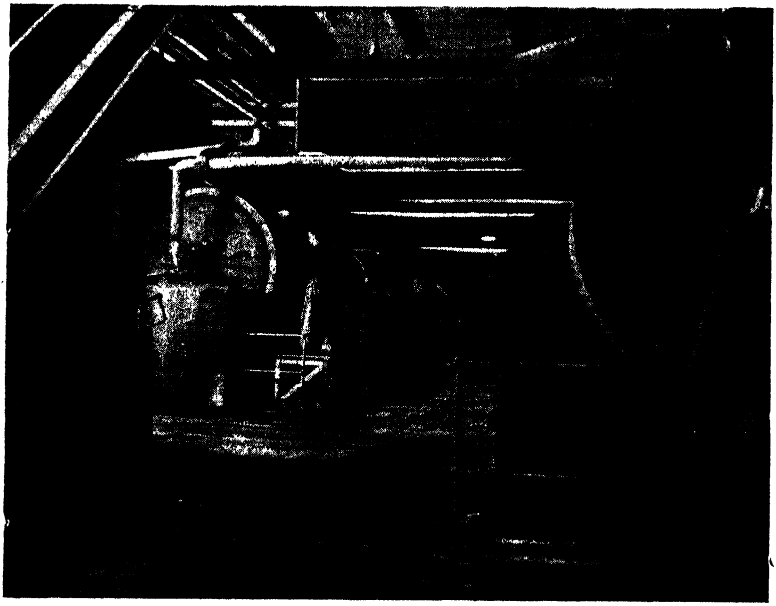


Fig. 78. Ball mills for the manufacture of urea-formaldehyde moulding powders[23]

For highly-filled moulding powders, the cellulose-urea resin mixture can be mechanically mixed with further cellulose, either wood flour or paper, to yield moulding powders with as much as 85 per cent cellulose filling. The use of cellulose as filler enhances the stability and ageing characteristics. It also eliminates the tendency towards crazing which is an outstanding defect of unfilled transparent urea-formaldehyde resin.

According to one patent[3], urea and formaldehyde are best mixed in the molecular proportions of about 1 : 1·5 under alkaline conditions in the cold. Cellulose fillers are incorporated with this alkaline resin and the mix is dried in 8 hours at 90° without causing the resin to react to the hardened condition. In one example 40 parts of formalin (36 per cent by weight) are heated gently in a glass-lined jacketed vessel and 0·2 per cent B.P. magnesium carbonate added. There is a slight degree of acidity which is neutralised by stirring for 2 hours. One part of 0·880 ammonia and 22 parts of urea are then added and the temperature allowed to reach only 20°. After a further 2 hours the temperature reaches 35° and the resin syrup has been formed.

Fig. 79. Moulding beakers[22]

Then 10 parts of the syrup are mixed at 40–50° for half an hour with 3 to 4 parts of disintegrated wood pulp of 10 per cent moisture content. The charge is dried at 90° for 8 hours and ground in a water-cooled ball mill with ½ per cent of mould lubricant (such as zinc stearate) and ½ per cent of a plasticiser; next, the powder is ground with 1 per cent of cinnamic acid.

Cinnamic acid has a melting point of 133° C. which would therefore only become active near the moulding temperature of the resin. This acid is not soluble to any marked extent so that it does not tend to dissolve in the water present in the resin, which would tend to cause incipient curing during storage.

According to Redfarn,[19] "ideally what is required is an inert substance which, when mixed with the powdered, dried, resin-filler material, has no action or solubility in the cold. At moulding temperatures the inert substance should liberate acid which should dissolve in the resin and catalyse the hardening."

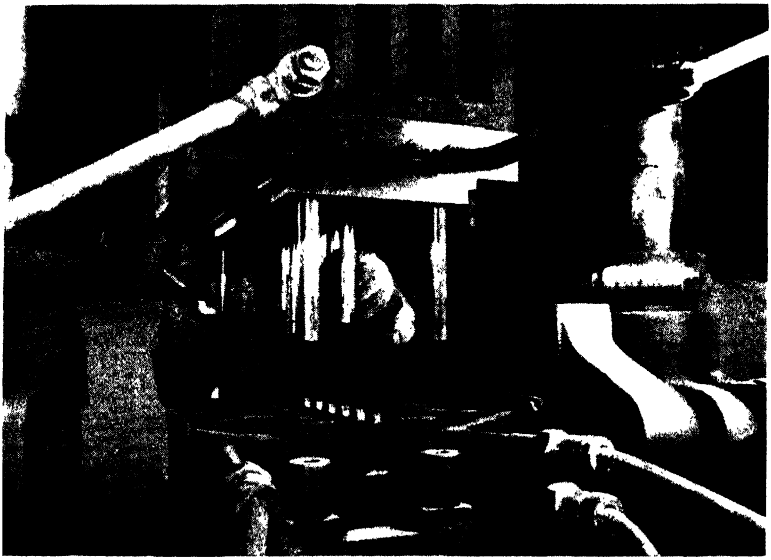


Fig. 80. Moulding Torch Cases[22]

The method employed by Imperial Chemical Industries, Ltd.,[11] has been described as:

Urea and formaldehyde are heated for 2½ to 3½ hours at pH 7·5–8. 306 parts of aqueous resin syrup is mixed with 174 parts of paper pulp, and dried in a rotary drier to 1–2 per cent free moisture. 0·2 per cent zinc stearate and 0·1 per cent cyclohexanol stearate are added to act as lubricants, and 1·0 per cent tri-ethyl phosphate as hardening catalyst. The addition of 1 per cent ammonium carbonate is recommended as stabiliser.

Another method described by Bakelite, Ltd.,[1] employs urea and formalin in the molecular ratios 1 : 1·5 (21 parts urea: 40 parts formalin) are heated to 80° C. in the presence of a small amount of ammonia (2·49 parts of 0·910 s.g.) or ethylene diamine (1 part) for 20 minutes and then cooled; 90 c.c. of N. hydrochloric acid added. The liquor is vacuum-distilled until half of the water is removed. The liquor is kept alkaline at pH of 8. It is mixed with 16 parts wood flour, lubricants, plasticisers, and colouring materials, and dried in a vacuum drier at 70° C. The material is treated on hot mixing rolls and is then disintegrated to give moulding powder.

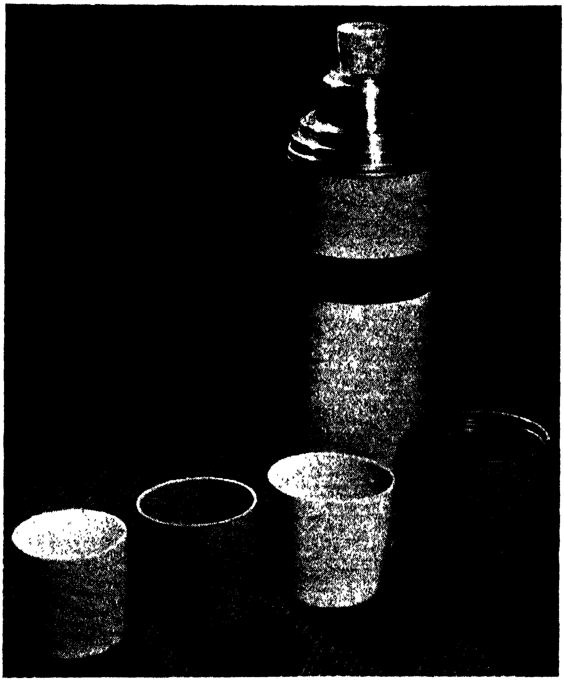


Fig. 81. Thermos bottle container with nesting cups made from Urea-Formaldehyde Resins[22]

In addition to urea, other derivatives such as thiourea and guanidine behave in a similar manner, and are fairly widely used for special purposes.

Urea Moulding Materials. The manufacture of urea moulding powders is admirably illustrated by the details available regarding production at the Dynamit A.G., at Troisdorf.

Three types of urea moulding material were made. These are Pollopas Normal, Pollopas Universal, and Pollopas Special.

Pollopas Normal

300 kg. formaldehyde (30 per cent) neutralised to pH 7 with NaOH
90 kg. urea (Pure A for lighter colours)
40 kg. thiourea
4·5 kg. NH_4OH (0·90 specific gravity)
0·03 kg. $MgCO_3$

A jacketed stainless steel or enamelled iron still fitted with a stirrer is used. The mixture is condensed at 40°–45° C. for 30 minutes. The pH of the mixture after condensation should be 7·0. If this is not correct it is adjusted with magnesium carbonate, but the batch is put on one side and gradually worked away. The syrup is filtered through a cloth bag into a stainless steel internal mixer. Here it is mixed with 105 kg. sulphite cellulose (this contains about 85–88 per cent α–cellulose, and usually 10–12 per cent water). The cellulose is in sheet form and is added in sheets, the workman simply breaking up the sheet and putting it in the mixer. When all the sheet has been added 0·95 kg. zinc stearate and 0·1 kg. $MgCO_3$ is added as stabiliser. The mixture is kept in the kneader for two hours at 45°–50° C. It is transferred to a mixer which breaks up any lumps.

The final process is carried out in ball mills. All mills above 1,000 litres capacity are water-cooled so that the temperature does not rise above 25°C. The charge of balls is 1,000 kg. porcelain balls to 1,200 kg. Pollopas. The balls are 70 mm. in diameter; 0·3 per cent zinc stearate is added, and the milling time is 60–100 hours. After addition of dyes, grinding is continued for seven hours, depending on the shade being made. For white materials only lithopone is used because titanium oxide causes the final material to turn yellow.

Another grade, known as Pollopas Universal, is made along similar lines:

300 kg. formaldehyde (neutralised)
120 kg. urea (pure for light colours and translucent grades)
5·4 kg. NH_4OH (0·90)
0·1 kg. ZnO

This is condensed for 20 minutes at 40°–45° C.—the pH is 6·2. Then 1·5 kg. hexa is added and refluxed for 10 minutes at 40°–45° C.—pH should be 7—if it is not 7 it should be adjusted by addition of more hexa, ZnO or $MgCO_3$. This is most important since an acid hardener is used. The process thereafter is the same as before. The resin solution is filtered to the mixer and 105 kg. cellulose and 0·5 kg. zinc stearate are added. After mixing for 2 hours the material is dried for 2½ hours.. The drying must be carefully done, as the flow properties are controlled by drying time. The material is ball-milled for six hours, during which

TABLE 53

GENERAL CHARACTERISTICS OF AMINOPLASTICS, MOULDINGS, SHEET AND TUBE[8]

Sample No.	Form	Colour	Ash %	Nature of Pigment and Mineral Filler	Specific Gravity at 20° C.	Water Absorption (24 hrs. at 20° C.) %	Loss on Heating (6 hrs. at 110° C.) %	Remarks
1	Moulding	Scarlet	5·0	Dyestuff, zinc oxide	1·50	0·33	2·2	Cellulose filled and colour
2	Moulding	Green	2·5	Aluminium lake, zinc oxide	1·48	0·28	2·6	
3	Moulding	Ivory white	2·0	Aluminium oxide	1·50	0·55	3·0	
4	Moulding	Ivory white	6·5	Zinc oxide	1·55	1·20	1·9	
5	Moulding	Ivory white	10·0	Zinc oxide	1·60	0·48	1·7	
6	Moulding	Ivory white	12·0	Zinc oxide	1·63	0·61	2·2	
7	Moulding	Blue	7·5	Ultramarine	1·54	0·18	1·9	
8	Brown	Moulding	0·7	Aluminium lake	1·44	0·48	3·5	
9	Moulding	Black	0·2	Aluminium lake	1·43	0·50	3·4	
10	Sheet	Green	6·1	Aluminium lake and zinc oxide	1·58	0·2	1·1	
11	Sheet	Cream	25·0	Siliceous earth	1·69	0·10	2·2	Wood filled and pigmented moulded sheet
12	Tube	White	17·7	Zinc oxide	1·64	0·65	2·35	Wood filled and pigmented moulded tube
13	Sheet	Green	6·8	Aluminium lake, zinc oxide	1·56	0·25	0·8	Wood filled and pigmented moulded sheet
14	Sheet	Green	2·2	Aluminium lake	1·50	0·3	1·8	
15	Sheet	Light blue	1·0	Dyestuff	1·49	0·3	3·3	
16	Sheet	Cream	24·8	Lithopone	—	0·13	2·0	

TABLE 54. PHYSICAL PROPERTIES OF MOULDINGS MADE FROM BEETLE, BEETLE TRANSPARENT, SCARAB AND POLLOPAS[8]

Test	Beetle	Beetle Transparent	Pollopas	Scarab
Specific gravity	1·49–1·63	1·425	1·50–1·60	1·45–1·60
Tensile strength in lb. per sq. in. cross-section	8,000–10,500	7,000–8,000	8,000–10,500	9,000–11,000
Ditto in kgm. per sq. cm. . .	560–730	490–560	560–730	630–760
Cross-breaking strength in lb. per sq. in.	13,000–16,000	13,000–16,000	14,000–17,000	13,000–16,000
Ditto in kgm. per sq. cm. . .	915–1,130	915–1,130	985–1,200	915–1,130
Impact strength on Charpy notched-bar test				
In kg. cm. per cm.^{2} . .	1·80–2·20	1·8–2·0	1·90–2·30	1·80–2·20
In ft. lb. per sq. in. . .	0·84–1·02	0·84–0·93	0·88–1·07	0·84–1·02
Water absorption				
(B.S.S. 488) 24 hours . .	30 mgm. (0·10%)	135 mgm. (0·45%)	18 mgm. (0·06%)	45 mgm. (0·15%)
7 days . . .	150 mgm. (0·50%)	—	80 mgm. (0·27%)	195 mgm. (0·65%)
Dielectric strength				
(1) At ordinary temperature .	17,000 volts per mm. (432 volts per mil.)	—	17,000 volts per mm. (432 volts per mil.)	17,000 volts per mm. (432 volts per mil.)
(2) Temperature of breakdown under a strain of 6,000 volts (A.C.) per mm. (152 volts per mil.)	70°–90° C.	70°–90° C.	70°–90° C.	70°–90° C.
Volume resistivity at atmospheric temperature—ohms per cm.^{3} .	10^{12}	—	10^{12}	10^{12}
Surface resistivity at atmospheric temperature—ohms per cm.^{2} .	10^{11}–10^{12}	—	10^{12}	10^{11}–10^{12}
Weight per cubic inch . . .	0·86–0·95 oz.	0·825 oz.	0·82–0·92 oz.	0·84–0·92 oz.
Apparent density of powder . .	0·50 (Densified, 0·70)	0·65	0·57	0·70
Moulding contraction . . .	·008 per linear inch	0·011 per linear inch	·008 per linear inch	·008 per linear inch
Coefficient of expansion . .	·000045 per °C. (·000025 per °F.)	—	·000038 per °C. (·000020 per °F.)	·000043 per °C. (·000024 per °F.)

flow properties are also tested. Then 0·8 per cent dichlorhydrin ($CH_2Cl—CHOH—CH_2Cl$) is added. This hardener is excellent, but must not be used for materials intended for use with hot liquids. The dichlorhydrin is neutralised to brom-thymol blue with N/2 NaOH. Where mouldings are to be used hot liquids $ZnSO_3$ is used (1·5 per cent). This is more difficult to disperse, so it is finely ground and sieved in. It does not cure so rapidly as dichlorhydrin. Storage life of this moulding powder is 6 months.

Another moulding powder, Pollopas Special, is made in the same way:

300 kg. formalin (30 per cent) (neutralise)
110 kg. urea, technical only because this material is only used pigmented
20 kg. thiourea
4·5 kg. NH_4OH (0·90)
0·03 kg. $MgCO_3$

This is condensed in exactly the same manner as Pollopas Normal. The pH at the end of condensation should be 7·0. The syrup is filtered and mixed with 105 kg. cellulose, 0·9 zinc stearate, and 0·1 kg. $MgCO_3$. The lubricants are added in the mill itself.

This is kneaded at 45°–50°C. for 2 hours and thereafter ball-milled.

The Properties of Urea Resins. Urea resins have a number of excellent characteristics. They are resistant to oxidation, to oil, grease, weak alkalis, weak acids, alcohol, and other solvents. They are very hard, resist abrasion and scratching, and possess high tensile strength. The resin flows under heat and pressure and then sets, a process which can be brought about quite rapidly. The moulded products are inert, have no taste and smell, and are consequently popular for domestic uses.

There is a complete colour range available, and the translucent materials in particular are widely used as lamp-shades and reflectors. Urea resins have excellent insulating characteristics, in particular they are non-tracking; this contrasts favourably with the phenol-formaldehyde resins. They are not so heat-resistant as the phenol-formaldehyde mouldings.

The moulding powders are generally moulded at much lower temperatures than phenol-formaldehyde resins, for example, between 140°C. to 155°C. Pellets are very extensively employed. However, because the moulding powders do not flow so well the pressures are much higher, ranging from 1½ tons to 3 tons per sq. inch. The time of cure is dependent upon the size and thickness of the moulding, ranging from 30 seconds to 12 minutes. Urea-formaldehyde resins char when they are overcured. They are corrosive, especially at high temperature. It is therefore desirable to use chromium-plated moulds.

Urea resins are never moulded in the same moulds as are used for phenolic resins because the moulds are poisoned.

The degree of cure of urea-formaldehyde mouldings is assessed by the behaviour in boiling water. Fully cured articles should not become chalky in appearance before 15 minutes immersion. When overcured they tend to discolour and darken.

Probably the best known mouldings made with urea-formaldehyde resins are for tableware. Cups, saucers, plates, etc., are made on the largest possible scale. They are attractive, light, and completely free from odour or taste.

These resins are favoured for electrical housings and electrical mouldings generally. They are far superior to phenolic mouldings because of the higher resistance to tracking. Another big outlet is the use as translucent lighting fixtures. We have become aware of them in this country, particularly for applications including tableware, bottle-caps, control knobs, cosmetic containers, etc.

Outstanding applications of urea resins, apart from moulding powder, are their use for coatings, their use as bonding agents, adhesives generally, and their use in the treatment of textiles.

The Application of Solutions of Urea Resins. The reaction between urea and formaldehyde can readily be stopped at various stages of resin formation. Thus it may be prepared as a colourless liquid; as a water-soluble product; in an intermediate rubbery condition, insoluble in water; or as a solid infusible insoluble material.

The initial solution is widely used as an impregnating medium for materials such as paper, cardboard, cloth, asbestos, etc. Such materials may be built into sheets, rods and tubes and applied together by heat and pressure. Alternatively, impregnated materials can be shaped and set.

Fillers can easily be incorporated in this fluid, the nature of the filler depending on the requirements. Thus cellulose or wood flour are the normal ingredients for moulding purposes, conferring flexibility and strength; mineral fillers such as clay, talc, whiting may be added; asbestos may be incorporated to make fire-resisting materials; and so on.

The behaviour of the resin solution can be controlled by the addition of various ingredients. Hardening can be accelerated or retarded. In general the addition of acids or compound showing acid reaction hastens setting. Usually weak acids or acid salts are used, e.g. tartaric acid, citric acid, ammonium chloride, etc. On the other hand, alkaline salts tend to retard the reaction. The application of these principles make it possible to add hardeners to obtain quick-setting cements, a technique which is very widely practised.

Aqueous solutions of urea resins are used for stiffening fabrics, hats, paper and so on, the usual procedure being to dry at 100°C. for a quarter of an hour and then press the final product.

A typical adhesive or laminating resin may be prepared as follows:

One part of barium hydroxide is dissolved in 160 parts of 36 to 40 per cent formaldehyde solution; 120 parts of thiourea are stirred in. A temperature fall is observed due to the negative heat of solution, followed by a rise due to chemical reaction. With initial temperature of 20°C. for the solutions the rise may be to 40°C., and cooling is required to maintain 40°C. maximum. A clear solution results when the reaction is complete, after about two hours. The solution keeps well, although it tends to develop slight acidity. This may be counteracted by the addition of 2 parts of 0·880 ammonia. Further, the solution can be held nearly neutral by saturating with carbon dioxide. This precipitates barium carbonate, which may be separated and forms ammonium carbonate, which acts as a buffer against increase in acidity.

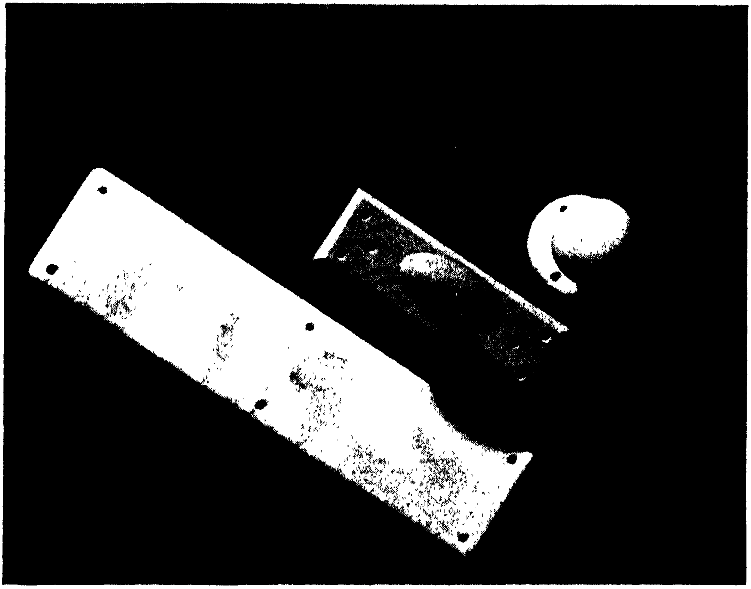


Fig. 82. Typical urea-formaldehyde mouldings

Application of Urea Resins to Textiles. Synthetic resins of the urea type are being used on a large scale in the treatment of textiles. The United States in 1947 used more than 8,000 tons for these purposes. The pioneers in this field were Tootal, Broadhurst and Lee, Ltd. By the use of the resins fabric may be modified in many ways. They improve resilience of rayon, the stability of cotton, the lustre of cotton, and the handle of many fabrics. They improve tensile strength, enhance wearing properties, increase elasticity, and serviceability, and so on. They improve resistance to creasing and reduce the tendency for shrinkage.

According to Powers:[15] "In tracing the development of synthetic resins for textile finishing, a great deal of credit goes to the Tootal, Broadhurst and Lee Company of Manchester, England, for the pioneer work in applying phenol-formaldehyde and urea-formaldehyde resins to cotton fabrics. They showed that unpolymerised urea-formaldehyde and phenol-formaldehyde resins could be impregnated and squeezed into the core of cotton and linen fabrics and, when polymerised in this position, produced fabrics with tremendously improved resilience. They further showed that if the surface or coating resin could be removed before it was polymerised, the resulting fabric was not stiffened and retained all of its initial suppleness, fullness, and drape. Millions of yards of fabrics containing 10 to 15 per cent of urea-formaldehyde resin are on the market to-day. In no case does the fabric or fibre show any evidence of resin coating, and the treated fabric is as soft as, and occasionally softer than, the untreated and less attractive type."

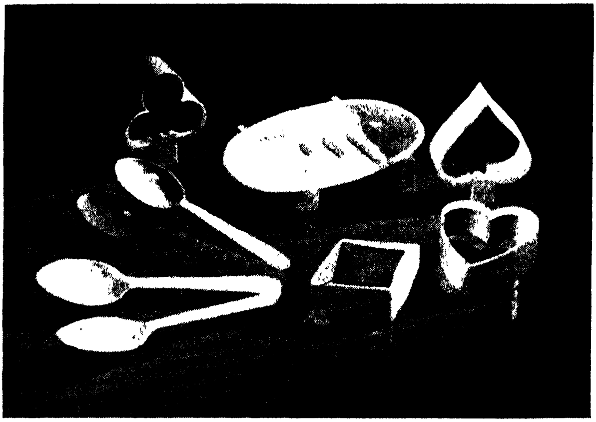


Fig. 83. Some domestic articles made in urea-formaldehyde moulding powder

These resins are widely used for treating fabrics and manipulating them. The methods have the charm of great simplicity. A typical solution is made up in the following manner:

A urea resin is prepared from 50 grams of urea and 200 c.c. of 40 per cent formaldehyde solution, which are boiled together for three minutes and then cooled; 4 c.c. of 33 per cent aqueous tartaric acid solution are added, and boiling continued for ten to fifteen minutes. The mixture is diluted with half its volume of water.

This solution is used to treat the fabric. Excess solution is squeezed out and the material is dried at 80° C. The material may then be shaped to any desired form and set by heating for a minute or two at 140° C.

An alternative resin for fabric treatment may be prepared from 50 grams of urea, 100 c.c. of formaldehyde, and 4·5 grams of 0·880 ammonia. These are boiled together for three minutes, followed by cooling and addition of 3 c.c. of 33 per cent tartaric acid solution, finally diluting with an equal volume of water.

Urea-Formaldehyde Adhesives. The outstanding field of application of urea resins at the present time is for adhesives. Expansion in the use of urea resin adhesives has been quite remarkable. In Germany the output of urea adhesives was stated to be 50,000 tons per year at the peak. In great Britain the leading firm alone produced 4,150 tons in 1945. American production in 1947 was over 20,000 tons! The resins can be used either cold or by hot-pressing methods. They are resistant to moisture, are unaffected by bacteria, fungi, high temperature and corrosive action. They have many advantages over other glues. The thermosetting characteristics are extremely valuable since they facilitate mass production use of the adhesives. They are particularly widely used for plywood manufacture. Their great importance lies in such fields as aircraft construction, boat-building, house construction, etc.

Urea-formaldehyde resins as adhesives are usually applied in the form of a concentrated aqueous solution, or syrup. A hardening agent, an acid or a salt, must be added which rapidly accelerates the setting. The most widely used hardening agent is ammonium chloride. Such materials are sometimes used without being diluted, where exceptional water-resistant joints are required. However, it is usual to extend the solution with a quantity of filler. For example, for ordinary plywood, where the flat surfaces will be brought into close contact, rye flour or a starch is used as filler. The proportion may vary between 5 per cent up to 300 per cent of the urea-formaldehyde resin. The ability to extend or load these resin adhesives has an important bearing on the cost.

In those cases where relatively thick layers of glue are necessary, often referred to as *gap joints*, specially loaded mixtures are employed. Fillers may include wood flour, plaster of Paris, silica, ground Bakelite, and so on. These have the effect of reducing shrinkage to a minimum and delaying any cracking. They also have the advantage of reducing the fluidity of the resin during pressing so that there is no undue penetration.

There are ready-mixed urea adhesives in powder form readily available at the present time. The only drawback is their inability to withstand storage over long periods, especially in unsuitable circumstances. The powder is dissolved in water and is ready for use.

The first urea resin adhesive was Kaurit Glue W. This material, a urea-formaldehyde liquid glue, was introduced by the I.G. Farbenindustrie about 1933, and it quickly acquired great popularity. This success was due to the fact that besides being well adapted to hot-pressing technique it could also be used at moderate temperature or even for cold setting work. In this country this was followed by Beetle Cement W.[2] There are now a number of proprietary materials.

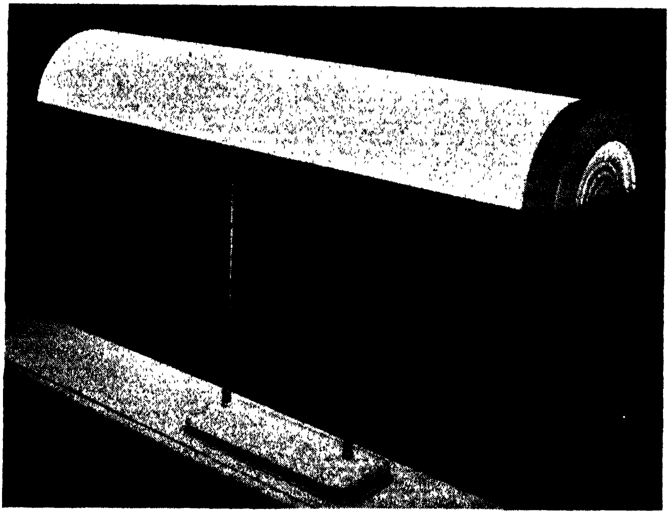


Fig. 84. A typical lamp reflector made from urea-formaldehyde

Kaurit W was made in the following manner:[24]

1 mol. urea
2 mols 30 per cent formaldehyde

were reacted together to form a 36 per cent resin solution, which was concentrated by heating at 65°C. *in vacuo.*

8–10 per cent rye or potato flour

was added, giving a mixture comprising

55 per cent resin
10 per cent flour
35 per cent water

This was brought to pH 7·0 with sodium hydroxide. By spray drying to moisture content of 2–3·5 per cent Kaurit W powder was obtained.

Methods of Use

The adhesives are always used in conjunction with a "hardener," which is either mixed with the glue just prior to use or applied to one of the surfaces to be joined, the adhesive being applied to the other surface. The function of the hardener is to bring about a chemical and physical change in the adhesive leading first to its gelatinisation and finally to setting. The hardener is usually a weak acid. The stronger the acid the more rapid will be the setting action.

Different hardeners are used according to the conditions available. In relation to plywood production, most requirements fall into the following categories:

1. Steam-heated presses operating at temperatures above 90° C.
2. Hot-water veneering presses operating at about 50° to 70°C.
3. Cold-pressing.
4. Oven heating for low-pressure laminating work.

The mixture of glue and hardener is applied thinly and evenly to alternate surfaces of the veneers comprising the plywood assembly. Spreading machines with finely-grooved metal or rubber rollers are generally used. The glue mixture may be applied to both sides of the centre-ply for three-ply work, or the two surface veneers may be spread each on one side only and an uncoated centre-ply interposed in assembly.

In the case of Kaurit Glues for hot press work, typical hardeners had the following composition:

1.	Ammonia (25 per cent)	27 parts
	Urea	45 parts
	Ammonium chloride	8 parts
	Water (boiling)	19·6 parts
	Methyl cellulose 5 Water 95	0·3 parts

Ten parts of this hardener with 100 parts Kaurit W had a pot life of 20 hours.

2. A faster hardener was as follows:

Ammonia (25 per cent)	20
Urea	30
Ammonium chloride	15
Water (boiling)	33·2
Methyl cellulose 5 Water 95	0·3

A typical formulation using this hardener was:

Hardener	20
Kaurit W	100
Potato flour	20
Wood flour	8
Water	100

Pressing times depend on the temperature and on the hardener selected. Pressure required may be as low as 40 lb. per sq. inch or up to 200 lb. per sq. inch, according to the plant available.

The ordinary hardeners give plywood with very good resistance to cold water, and samples of plywood have been kept for years exposed to the weather without any delamination or failure of the glue layer.

The use of urea resin adhesives in plywood manufacture has been greatly expanded because it can be extended with other materials. For many purposes there is no need for a cement which is fully waterproof, and in such cases the resin syrup is extended with rye flour. This reduces costs appreciably, whilst still giving a glue line of excellent strength. The water resistance of such joints is not so high as that of those made with the pure cement, but is better than is obtained with many other adhesives.

Liquid urea adhesives tend to become viscous after long standing. Consequently other types have been developed. Urea resins in the form of powder are available. The dry powder may be kept for over a year provided that it is kept cool, and it only requires to be mixed with the appropriate quantity of cold water to regenerate a liquid glue having all the desirable properties of the resin syrup. The liquid glue thus formed is used with hardeners, exactly as before. There are a number of other excellent proprietary types of urea-formaldehyde adhesives available at the present time.

The principal technical advantages of urea resin adhesives in the manufacture of plywood are:

1. Low pressure and low temperature pressing conditions enable many ordinary veneering presses to be used in the production of high-quality plywood.
2. Ordinary air-dried veneers are being used with complete success, irrespective of slight differences of 1 or 2 per cent moisture content. Urea resin adhesives are initially water soluble, therefore strict control of moisture is not necessary.
3. Owing to the lower temperatures and pressures employed, urea resin bonded plywood suffers little "burnishing" or "case-hardening" of the surface veneers. Consequently it is easy to glue in subsequent operations and does not require sanding to

open up the surface. This is of considerable importance in aircraft construction.

It is interesting to consider procedure in connection with plywood manufacture. When using the cold process a typical procedure is for one side of the joint to be coated with the appropriate hardener and allowed to dry. The other joint face is then coated with a very thin film of the cement, and after a period of about 15 minutes the two joint faces are brought into contact and clamped together by any suitable mechanical means (e.g. "G" clamps). Pressure is maintained for 2 to 24 hours, depending upon the hardener used.

When the hardener is mixed into the resin then the mixture has a very limited pot life.

TABLE 55

POT LIFE OF UREA RESINS AT DIFFERENT TEMPERATURES

Temperature	Slow Hardener	Fast Hardener
15°C.	12 hours	6 hours
20°C.	6 ,,	2½ ,,
25°C.	2½ ,,	1 ,,

Three pounds of urea glue per 100 sq. ft. is usually sufficient. About 1 lb. of hardener is required, and the time for drying is generally about half an hour. Too much glue results in longer drying periods being required.

In the hot process, the hardener is actually mixed with the cement before being applied to the joint. The hot process is recommended where it is essential that the joint should be waterproof. The joints obtained by the hot process will withstand even boiling water for long periods. Cold process joints will withstand water at ordinary temperatures almost indefinitely. There are two leading types of hardener supplied, one for use when the joints must be waterproof, and one for joints which will even be resistant against boiling water.

To give maximum water resistance, the Germans used a special hardener comprising:

Resorcinol	90 parts
Ammonium chloride . . .	10 parts

Depending on water resistance required, 10–25 of this powder is used with 100 parts Kaurit W liquid.

The method of using urea glues with the hot process is as follows:

(1) The hardener is mixed thoroughly with the cement. The mixture can then be kept for 30 hours at room temperature.

(2) The mixture is applied thinly to the joint faces which have previously been roughened with sandpaper; 2½ lb. of mixture is usually sufficient for 100 sq. feet.

(3) Pressing is carried out at a pressure of some 30 lb./sq. in. at a temperature of 90–100° C. The basic times in the press are 5 minutes with the hardener for waterproof joints and 8 minutes for the hardener designed to give maximum water resistance. One minute per millimetre of board thickness must be added to these basic times.

Urea resin films are not continuous but of porous structure. This is due to the fact that they are deposited by evaporation of water. De Bruyne[4] has utilised this fact in an ingenious manner. In general, far more adhesive is used than is really necessary. He therefore prepared urea adhesives as a foam.

Ordinarily urea resin adhesives have some disadvantages. Thus urea adhesives cannot be used for very thin plywood because thin veneers of wood are severely swelled by the water present, they tend to buckle and the resin penetrates too far when pressure is applied. Foam glues overcome this difficulty. This Aerolite foam glue has all the good properties of liquid resins but is much cheaper.

The idea behind this process is that, provided penetration of the glue into the veneers is obviated, only a very thin film of glue is needed to make good joints, and the amount of glue applied by any ordinary means (glue spreaders or brushes) is in excess of the optimum amount. By using the glue in the form of a foam of about the same consistency as the lather produced from shaving-soap, an extremely thin, uniform spread is obtained although the glue layer has an appreciable thickness. Actually the volume of the glue is about doubled by a special beater machine before it is poured into the glue spreader. Under ordinary factory conditions, without taking any special precautions, it is possible to get a spread of 1·35 lb. of glue per 100 square feet.

Details are available about the foam glue used in Germany.[25] A special foam-forming hardener was added to Kaurit glue. The hardener was:

Ammonium bicarbonate	60 parts
Ammonium chloride	22·5 parts
Wood flour	17·3 parts
Colour	0·2 part

These were mixed together as fine, dry powders. The glue mixture to be foamed comprised:

Kaurit W liquid	1,000 parts
Foam hardener	120 parts
Casein	9 parts
Wood flour	15 parts
Potato starch	60 parts
Water	600 parts

The casein and hardener are mixed together with 400 parts boiling water. The other ingredients are mixed together cold and added. When foamed, the volume is 2·5 to 3 times the volume of liquid.

Because of the nature of the foam it can be used with thin veneers without producing excessive wrinkling or causing overlap in the cores. The foam is allowed to dry on the veneers after it has come through the rollers of the glue spreader. It does this very quickly and, in fact, the film of foam will be found to be dry by the time that the veneers have been assembled for pressing.

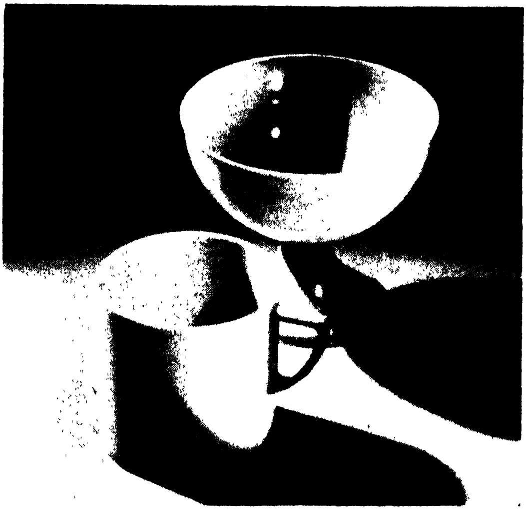


Fig 85 Typical urea-formaldehyde mouldings[22]

The press temperature required is 90° C., so that steam-heated presses are unnecessary and the older type of press so common in this country with hot-water heating can be used. The use of pressing temperatures below 100° C. obviates any risk of overheating of the wood with its attendant troubles.

Cold Setting Glues. Latterly, cold-setting urea resins cements have gained wide usage. These are generally liquid resins which may be used in conjunction with a hardener in the cold, and which set comparatively rapidly. They are often used with fillers to fill up interstices and so on.

The German hardener for cold-setting work had this composition:

Ammonium chloride	99·9 parts
Dyestuff	0·1 part

A yellow was used for furniture, red for most other applications.

Cold Hardener A	15 parts
Water	78 parts
Alcohol	6 parts

This hardener is applied to one side of the veneer and allowed to dry at ordinary temperature. The other side is coated with Kaurit W, and they are then pressed together. Setting takes 3 hours at 20° C., 10 hours at 15° C., and 24 hours at 10° C.

It is interesting to observe that ammonium salts predominate as hardening agents, notably ammonium chloride and ammonium thiocyanate. Among other salts, ammonium sulphate has been proposed by Dearing for incorporating into ready-mixed powder adhesives to give particularly good storing properties.

The Use of Urea Resins in Coatings. Urea resins have acquired great popularity for making lacquers and varnishes in recent years. They are used in very large quantities. Perhaps the most important point about this application is the fact that they are miscible with the alkyd resins, which are notably improved by their presence. Their use is closely bound up with alkyd resins. The resins ordinarily prepared in aqueous media are not found to be suitable for use in preparing these coating materials. It is found necessary to prepare the urea formaldehyde resins in the presence of alcohols. When this is done a number of alcoholic groupings appear to be formed in the resin which enables it to dissolve in many organic solvents. They also make it compatible with other resins. For such uses the resin is supplied in alcoholic solution as a viscous liquid. In this condition the resins are still reactive and thermosetting. The conversion to the infusible insoluble state is carried out by baking, the solvent being previously removed.

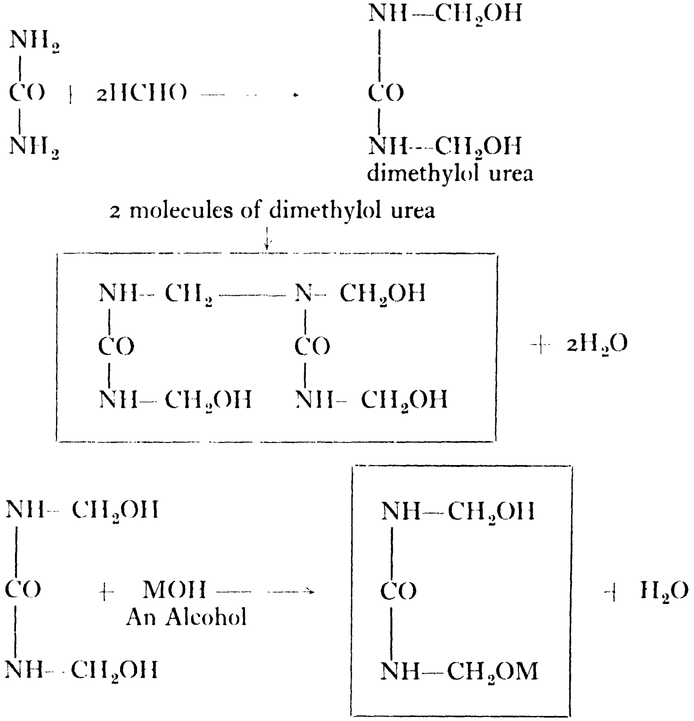
The reaction is considered to occur along the lines shown in the diagram on the opposite page.

These then react to form soluble resins.

In the synthesis of these urea resins intended for coatings, certain important factors are outstanding. These may be summarised as follows:

(*a*) Molecular proportions of reactants,
(*b*) Reaction temperature and times,
(*c*) Nature and amount of catalyst,
(*d*) The type of reacting alcohol, etc.

A great deal of work has been carried out in this field of activity. The action of typical alcohols is of great interest. It has been shown, for example, that with aliphatic alcohols, as the chain length increases so the solubility in hydrocarbons increases. Other characteristics are also affected. At the same time they become more compatible with tung oil and alkyd resins. The final film takes longer to cure, and is not so hard, but has better resistance to alkali.



$$\begin{array}{l} NH_2 \\ | \\ CO \\ | \\ NH_2 \end{array} + 2HCHO \longrightarrow \begin{array}{l} NH-CH_2OH \\ | \\ CO \\ | \\ NH-CH_2OH \end{array}$$

$$\downarrow$$

$$\boxed{\begin{array}{ll} NH-CH_2 & \!\!\!\!\!\!\!\!\!\!—N-CH_2OH \\ | & | \\ CO & CO \\ | & | \\ NH-CH_2OH & NH-CH_2OH \end{array}} + 2H_2O$$

$$\begin{array}{l} NH-CH_2OH \\ | \\ CO \\ | \\ NH-CH_2OH \end{array} + \underset{\text{An Alcohol}}{MOH} \longrightarrow \boxed{\begin{array}{l} NH-CH_2OH \\ | \\ CO \\ | \\ NH-CH_2OM \end{array}} + H_2O$$

At the present time the best combinations of properties have been obtained by the use of normal butyl alcohol, primary octyl alcohol, and secondary octyl alcohol. Polyhydric alcohols, such as glycerol, have not given very satisfactory results.

The behaviour of the alcohol groups during the reactions is not quite clear. Some are lost in the baking, others are retained.

Straight urea coatings are not particularly satisfactory, tending to be brittle and having poor adhesion. The best characteristics of urea resins for coatings are brought out by using them together with alkyd resins. In the usual way equal proportions of each type of resin are employed. The resulting films bring out the best characteristics of each type of resin. The outstanding adhesion, flexibility, and durability of the alkyd resin is supplemented by the hardness, the speed of setting and the heat stability of the urea resin.

Another outstanding feature of the urea-alkyd resin lacquers is the fact that the baking schedule can be carried out at very low temperatures for a short time. Colours are not affected, so that the lightest pastel shades can be attained.

The use of such resins in baking enamels has acquired great importance as baking enamels. Since there is no darkening, they are available as excellent pastel shades, and even in white. This type of enamel is employed for many widely-used products such as refrigerators, hospital equipment, metal furniture, industrial equipment and hardware.

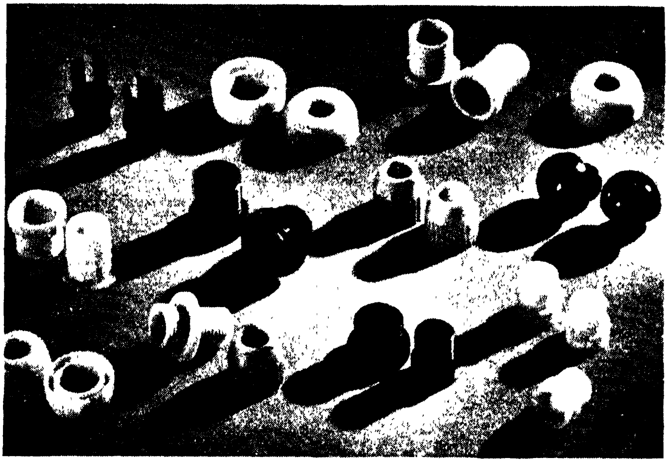


Fig. 86. Lamp accessories moulded from urea-formaldehyde powders

In many cases the baking process now used is based on infra-red radiation, which has proved to be much more effective and rapid.

Other applications where coatings based on urea resins have been used are for motor-bodies, cycles, machinery, and indeed all articles able to stand up to baking temperatures. Many war applications were of great importance. These resins were widely used for coating shells, bullets, etc.

REFERENCES

1 Bakelite, Ltd. B.P. 518,321/1940.
2 Beetle Cement. British Industrial Plastics, Ltd.
3 British Industrial Plastics, Ltd. B.P. 429,201/1933.
4 De Bruyne. Technical Literature, Aero Research, Ltd.
5 Einhorn and Hamburger. *Berichte*, 1908, **41**, 24.

6 Goldschmidt. *Berichte*, 1896, **29**, 2438.
7 Goldsmith and Neuss. B.P. 208,761/1922.
8 Halls. *Plastics*, 1942, **6**, 267.
9 Hodgkin, Hovey and Ryan. *Ind. Eng. Chem.*, 1940, **32**, 334.
10 Holzer. *Berichte*, 1884, **17**, 659
11 I.C.I. Ltd. B.P. 506,003/1939.
12 John. U.S.P. 1358834/1920.
13 Mittasch and Raustetter. G.P. 409,847/1922.
14 Pollak. B.P. 171094/1923.
15 Powers. *Ind. Eng. Chem.*, 1940, **32**, 1543.
16 Redfarn. *British Plastics*, 1933, **5**, 239
17 Redfarn. *British Plastics*, 1942, **14**, 11.
18 Redfarn. *Synthetic Resins and Allied Plastics*, Oxford University Press, London, 1943, p. 179.
19 Scheibler, Trostler and Scholz. *Z. angew. Chem.*, 1928, **41**, 1305.
20 Tootal, Broadhurst and Lee, Ltd. B.P. 437,361.
21 Walter and Gewing. *Kolloid. Beih.*, 1931, **34**, 163.
22 Photographs by courtesy of British Industrial Plastics, Ltd.
23 ,, ,, I.C.I. Ltd.
24 C.I.O.S. XXXIII-23, p. 50.
25 C.I.O.S. XXX-III-23, p. 77.

CHAPTER IX

MELAMINE-FORMALDEHYDE RESINS

PHENOL-FORMALDEHYDE resins and urea-formaldehyde resins have for some time had the field of moulding resins to themselves. During the last few years a new class of thermosetting synthetic resins has appeared. These are the melamine-formaldehyde condensation resins, now generally referred to as the *melamine* resins. They have a number of valuable characteristics which assure them of a wide field of application. They are making notable headway as moulding materials in the United States. About 17 million pounds melamine resins were used in the U.S. in 1947.

While having many features in common with the urea-formaldehyde resins, they show superiority in such factors as water resistance, heat resistance, light resistance, and more rapid setting characteristics. Although of comparatively recent origin they have already attained some importance. There is a tremendous usage for dishes in the United States.

Melamine resins and plastics based on them have only been commercially available since 1939. Switzerland led the field in this development, and the work has been carried forward in this country, in Germany,[4] and in the United States. It is interesting to note the rapidity with which the actual commercial development came about. An illustration is the fact that in 1938 the chemical, melamine, was valued at about £10 per lb. Inside twelve months the scale of production had grown so that the price had dropped to the order of 3/- per lb.

These resins have acquired popularity in particular for coatings. They have also specific characteristics which makes them of interest for moulding, and similar factors have led to their use for lamination, etc. As the applications have increased, so the cost has come down. The technique for the preparation of the chemicals involved has been well developed. As a consequence, melamine is obtained from raw materials which are in very free supply.

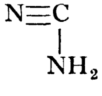
Historical and Chemical Backgrounds. Melamine is not a new material. It was first discovered by Liebig[8] in 1834. He heated potassium thiocyanate and ammonium chloride together, and heated the product with sodium hydroxide for some time to get melamine. The time was not ripe for any application. In fact, it is only during the last few years that the material has come out of the laboratory. It was never previously available in sufficient quantity and at a cost which might make it of interest for use in a synthetic resin.

Melamine is actually obtained from calcium carbide, i.e. from coal and limestone. It is evident, therefore, that the raw materials for melamine are available in very large quantities. In the first place calcium carbide is converted to calcium cyanamide by heating with nitrogen from the air. This material is widely used as fertiliser since treatment with water causes it to give off ammonia. It is also employed in the hardening of steel and for various other less important purposes. It has been found that calcium cyanamide can easily be converted into dicyandiamide, which is a grey powder. The dicyandiamide is obtained from calcium cyanamide simply by boiling with water. Dicyandiamide has also found application as a plasticiser.

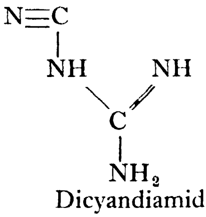
There are a number of methods for converting this into melamine. The outstanding method appears to be to heat dicyandiamide with liquid ammonia under pressure. In due course the ammonia is released and recycled for further use. Other methods have been developed.

Properties of Melamine. Melamine is a white crystalline compound soluble in water, melting at 354° C. Its molecular weight is 126. It has a specific gravity of 1·57. When heated strongly it gives off ammonia and yields a yellow powder. It tends to sublime just before it melts. According to McLellan[10] the solubility in water is 0·5 per cent at 25° C., and 5·5 per cent at 90° C. Melamine is slightly soluble in alcohol, and quite insoluble in inert solvents. It is slightly soluble in glycol and glycerol. It is a weak base.

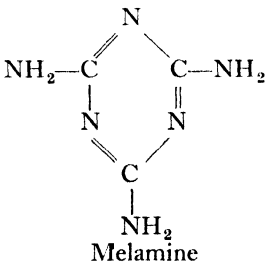
Melamine may be considered as a polymer of cyanamide. Chemically it is 2.4.6—triamino—1.3.5—triazine. Cyanamide is $CN.NH_2$; melamine is $(CN.NH_2)_3$. Melamine may be considered as the trimer of cyanamide, CH_2N_2, of which dicyandiamide is the dimer. These relations may be shown pictorially by the commonly accepted structural formulae:



Cyanamide



Dicyandiamide



Melamine

Melamine is a comparatively reactive material. It reacts with aldehydes, alcohols, sugars and phenol. The outstanding reaction which has led to the production of synthetic resins is with formaldehyde. It dissolves readily in formalin when heated, forming methylol-melamines, which can be separated by evaporation at low temperature. If heating is continued condensation occurs with the production of a synthetic resin. Under suitable conditions a water-white synthetic resin is produced which is soluble in water and alcohol. These resins have gained importance in the following fields and in this sequence:

(*a*) as a coating material,
(*b*) for the impregnation of wood and the preparation of adhesives for laminated materials,
(*c*) for the preparation of new moulding powders.

Preparation of Melamine. Preparation of melamine is usually carried out on a commercial scale in the presence of anhydrous ammonia under a pressure of 10 to 100 atmospheres at temperatures varying from 100°C. to 400°C., In actual practice the reaction is carried out either by batch or continuous process. Although melamine is usually made under high pressure, it may be prepared at atmospheric pressure. This has been found possible by employing a mono- or dialcohol amine as a combined solvent, heat buffer, and condensation catalyst.

In the processes involving the production of melamine from dicyandiamide, varying quantities of other related nitrogenous compounds are formed.

Most methods for the manufacture of melamine are based on the conversion of dicyandiamide to melamine. In recent years there has been an increasing number of patents dealing with this aspect. According to McLellan, melamine is formed when cyanamide is heated at about 150°C. It is also formed when dicyandiamide is heated above its melting point of 209°C.

The experimental preparation of melamine may be carried out in the following way : 300 grms. of dicyandiamide is placed in a 2 litre beaker. This is carefully heated on a hot plate. The mass begins to melt, and a vigorous reaction occurs. Copious fumes are given off which contain ammonia and sublimed melamine. The temperature may rise as high as 350°C. before the reaction finishes. The contents of the beaker may be leached out and crystallised. In this way almost pure melamine is obtained.

Another method for preparing melamine is to heat dicyandiamide with concentrated ammonia for three hours at 120°C. when a yield of about 35 per cent is obtained. The Ciba Company[2] of Basle obtained patents for preparing melamine by heating dicyandiamide with anhydrous ammonia in an autoclave. In one example, 7 kilos dicyandiamide and 6 litres methanol were mixed in an autoclave with stirring.

Ammonia was forced in until the pressure reached 3 atmospheres. The temperature was taken up 100°C. to 150°C. by 10 degrees each hour. After 12 hours reaction was completed, the material was filtered and washed giving a yield of 83 per cent melamine.

The I.G.[6] prepared melamine by heating dicyandiamide in an autoclave with solutions of ammonia in alcohol or ketones. Jayne[7] dissolved dicyandiamide in monoethanolamine. Equal parts were heated in open vessels. The dicyandiamide dissolved and at 140°C. an exothermic reaction commenced, so that the temperature rose to 170°C. After cooling down the mixture was diluted with water and washed thoroughly, giving a very high yield of pure melamine.

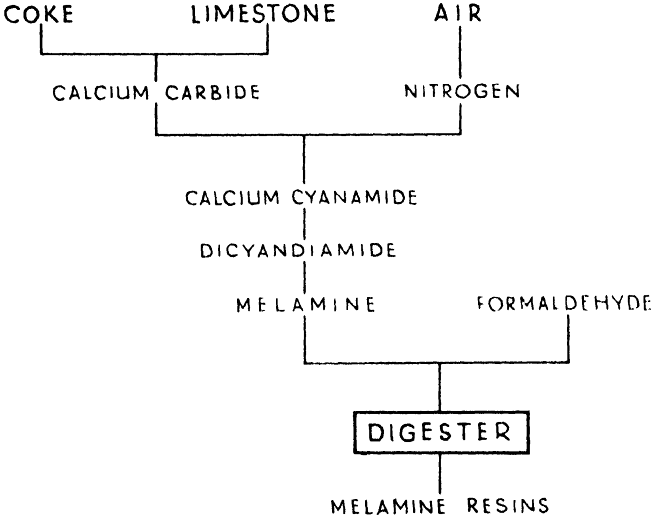


Fig. 87. Flow sheet for melamine resins

McLellan has summarised his extensive work on the subject as follows:

1. Pyrolysis of anhydrous cyanamide, guanidine salts alone, and dicyandiamide, in the open or in the presence of solvents at atmospheric pressure, does not give rise to high yields of melamine.
2. Heating dicyandiamide and guanidine together, either dry or in the presence of ammonia, improves the yield or hastens the reaction or does both.
3. Heating dicyandiamide under pressure in the presence of free ammonia gives high yields of the desired product.
4. Heating cyanamide and dicyandiamide in equimolecular proportions in an autoclave in the presence of ammonia does not

greatly enhance the yields or speed of reaction over that normally obtained with dicyandiamide in ammonia.

5. When dicyandiamide is heated under pressure with free ammonia, the presence of cyanamide, guanidine, and biguanide can be demonstrated.

Ammeline and ammelide impurities in the product, being insoluble, may be removed by recrystallising the melamine from water. Cyanuric acid salts such as melamine cyanurate, are relatively insoluble; all such by-products may be re-processed in the reactor with ammonia under the melamine synthesis conditions, to give additional quantities of melamine.

In a recent patent Du Pont de Nemours described how to make melamine by heating urea or related compounds with ammonia at elevated temperatures.[3] The preferred reaction conditions include a temperature range of 300° to 400°C., a pressure of 200 to 450 atmospheres, and a molar ratio of ammonia to urea between 4 : 1 and 20 : 1. However, with pressures between 600 and 1,000 atmospheres, this ratio may be less than 4 : 1. A reaction period of 10 minutes is generally sufficient to give about 60 per cent conversion.

Besides its ability to withstand pressure, the reaction vessel should be lined with material which is not corroded by the reactants, and which does not catalyse the decomposition of ammonia. A convenient apparatus is a silver-lined bubble-plate column through which ammonia and urea flow in countercurrent. Molten urea at 140°C. is pumped into the top of this column, while ammonia is injected at the bottom. A hot let-down valve, preferably operating at 350°C., permits removal of the non-gaseous products, while gases are withdrawn from the top of the column.

Melamine is fairly reactive and forms a number of condensation products. The most important of these are the methylol compounds. They are obtained when melamine is treated with neutral or slightly alkaline formaldehyde, or with some substance producing formaldehyde. Six products are possible from the condensation of these two compounds. The most stable is hexamethylolmelamine, which may be readily prepared. This compound may be produced by heating melamine with an excess of neutral formaldehyde at 90°C. Another method is to allow the melamine to react with neutral formaldehyde at room temperature over a period of 15 to 18 hours. The product formed is the same and contains one molecule of water of crystallisation per molecule of hexamethylolmelamine.

The methylol compounds of melamine behave in many ways like complex alcohols. For example, they can be esterified. This is of interest to the resin chemist, for there are complex polyhydric alcohols, which, different from many of the more common alcohols, are resistant to discoloration at high temperatures. Under favourable conditions the methylolmelamines can be reacted with polybasic acids to form complex resinous esters. When such reactions are carried out in the presence of an oil or fatty acid, resins of the alkyd type are produced.

Resins from Methylolmelamines. Most of the common resins now available are produced by direct condensation of melamine and formaldehyde. These condensation products, like those of dimethylolurea, may be divided into three classes—water-soluble, hydrocarbon-soluble, and insoluble. The water-soluble and insoluble condensation products may be considered as different stages of the same reaction. The hydrocarbon-soluble types are somewhat different in character.

The reactions resulting in the production of these three classes of compounds are controlled by four general factors—namely, ratio of components, catalysts employed, time of reaction and temperature. By adjusting these conditions the size and complexity of the condensation unit of the final product can be controlled. Under suitable conditions the methylolmelamines, in common with dimethylolurea, form three-dimensional heat-convertible resins.

A melamine resin may be prepared by adding 126 parts melamine to 162 parts formaldehyde (37 per cent) which has been adjusted to a pH of 7·2 to 9·0 with the aid of a little caustic soda. The syrup then obtained, after heating in a reflux apparatus for 10 minutes, is sprayed at the rate of 10 pounds per minute into a hot-air drier kept under a two-inch vacuum, the white resin powder being continuously discharged at the same time.

These materials are somewhat more complicated than those of dimethylolurea, but are probably formed by similar mechanisms. There are two linkages which may exist between molecules of methylolmelamine under these conditions—the ether linkage and the methylene linkage.

The following methods for preparing resins suitable for laminating purposes have been described in a recent patent of the American Cyanamide Co.[1] To 480 parts by weight of 73 per cent formaldehyde solution was added sufficient 2N NaOH to give a pH of 9·55 (using a glass electrode). To this alkaline formalin, 168 parts by weight of dicyandiamide and 31·5 parts by weight of melamine were added. The whole mixture was heated under reflux until boiling started, which took 14 minutes. At this time the whole mixture was water-clear and was then kept at the boiling point under reflux for an additional 30 minutes. (The ratios of the components were 1 mol of dicyandiamide to 0·125 mol of melamine to 3 mols of formaldehyde). After this period a viscous syrup was obtained which remained clear on cooling, but if diluted with water had strongly hydrophobic properties.

Another example given was: Five parts by weight of guanidine carbonate were dissolved in 500 parts by weight of 37 per cent formaldehyde solution. The pH was 9·22 (with the glass electrode). 140 parts by weight of dicyandiamide and 55 parts by weight of melamine were added and dissolved during heating up to the boiling point. The ratio was 1 mol of dicyandiamide to 0·25 mol of melamine to 3·6 mols of formaldehyde. The mixture was kept boiling under reflux for 35 minutes to give a syrupy condensation product.

Another interesting and informative description involving the use of melamine and dicyanamide has been given in a recent patent specification.

420 parts dicyandiamide (1 mol)
158 parts melamine ($\frac{1}{4}$ mol)
810 parts 37% formaldehyde (2 mols)
0·24 part sodium hydroxide.

The dicyandiamide and melamine are dissolved in the formaldehyde solution to which the sodium hydroxide is previously added. The mixture is heated to about 70° C. until a clear, homogeneous solution is obtained. This water-clear solution having a pH 8·1 (glass electrode) is allowed to react at 50° C. for 6 hours. The substantially clear solution of the reaction product is then cooled to room temperature, whereupon the condensation product becomes a creamy white mass. This creamy product may be heated and at about 50° C. becomes again a water-clear solution which again forms the cream upon cooling to room temperature. If desired, the solution obtained by heating the cream may be diluted to any degree by the addition of any desired proportion of water of about the same temperature as the solution. The diluted solution can be used for impregnation or any other desired purpose. This cream may be kept over a long period of time during which it may be diluted with water as described.

In order to determine some of the properties of this cream, it was diluted with an equal quantity of water and the dilute solution was used to impregnate sheets of all-cotton paper (·007 in. thick). This was done by dipping the sheets in the solution and then allowing them to dry at room temperature (25° C.) for about 36 hours, after which the sheets were further dried by placing them in a drying oven for about 5 minutes at 70° C. Five of the dried sheets so treated were stacked and the stack placed between stainless steel plates, the whole assembly then being placed in a suitable hydraulic press. The temperature of the press was raised to 140°C.–145°C., and pressure kept at 1,125 lb. per sq. inch for 30 minutes. The press was then allowed to cool and there resulted a homogeneous, translucent laminated sheet having high gloss. A sample of the laminate sheet showed not the slightest sign of delamination or disintegration after 30 minutes' immersion in boiling water. The laminated sheet contained about 61 per cent resin, was ·032 in. in thickness, and after the 30-minute boil was found to have absorbed 7·7 per cent water.

Applications of Melamine Resins. Unmodified resins find application as textile and paper coatings and as adhesives. They are particularly useful in making impregnated paper having high wet strength. The water-soluble melamine-formaldehyde resins which have been modified by the addition of such compounds as glycerol, glycols, or simple sugars, are of considerable commercial importance.

Moulding compounds can be produced by slightly modifying the conditions. The finished products are characterised by high softening point, rapid moulding cycle, and good mechanical strength. They have the advantages of both phenolic resin and urea resin. These products can be further modified by the addition of fillers such as α-cellulose, wood, flour and pigments. A slight change in formulation enables the production of casting resins of exceptional clarity and water resistance.

Melamine Powders Based on Melamine Resins. In the form of moulding powders—that is, combined with alpha-cellulose pulp—a material is produced similar in appearance to urea moulding powder. It is moulded in the same manner, and in the moulded form, is almost identical in appearance. However, the moulded melamine-formaldehyde resin is considerably harder, more heat-resistant, shows greater resistance to dilute acids and alkalis, and has a lower water absorption. The products are odourless, tasteless, and inert. They withstand hot water.

Melamine moulding powders may be worked without special moulds and at moderate temperatures. In addition the cured resin possesses intrinsic properties of great value which assure it of very wide fields of application. Melamine resin is supplied in the form of a fine powder and should be stored in a cool dry place in well-closed containers, in order that its flow properties may be maintained for a long period. It should be noted that production of the moulding powder appears to be confined, for the present, to the United States and Germany. Melamine materials are not sensitive to hydrogen peroxide, whereas urea materials are.

Hardened steel dies are required for moulding, but owing to the fact that the moulding powder is neutral and inert they need not be made of corrosion-resisting steel, nor need they be chromium plated. There is no effect on metallic inserts. The usual moulding pressure should be about 4,000 lb. per square inch. Curing temperatures cover the wide range from 130–165°C. The most suitable values for temperature and time, particularly in the case of components possessing varying sections, is best determined by experiment on test pieces in the usual way. Prolonged over-curing has an adverse effect upon the mechanical properties.

In working up the new resin, the various devices found of value in connection with urea and thiourea resin may be applied. Thus, in the case of tooled thin-walled objects, such as beakers, cups, etc., it is recommended that the powder, after filling the mould, be warmed for 20–30 minutes at 90–100°C. The loose powder compacts by this heating and more complete homogeneous flow during pressing is attained.

Flat objects, such as plates and so on, may be moulded quite satisfactorily without pre-warming, if the mould is allowed to stand for about 10 seconds after closing.

Moulded objects from melamine resin are characterised by their high resistance to the effect of dry heat, hot water and hot beverages, such as coffee and tea, and are usually free from all taste and smell.

Melamine moulding powders have very good electrical properties. On account of its high resistance to tracking, melamine resin is particularly valuable in connection with high tension current work as an insulating material.

TABLE 56

PROPERTIES OF MOULDED MELAMINE RESINS FILLED WITH α-CELLULOSE

Specific gravity	1·5
Tensile strength	7,000 lb./in.^{2}
Compressive strength . . .	30,000 lb./in.^{2}
Flexural strength	15,000 lb./in.^{2}
Impact strength (Izod) . . .	0·3 ft. lb. per inch of notch
Water absorption (7 days at 20°.) .	1·5 per cent
Dielectric strength	350 volts per mil.
Volume resistivity	10^{12} ohms per cubic cm.

Combined with the good electrical characteristics this has led to the use of melamine moulding powders for making electrical parts which have to withstand unusually high temperature conditions, e.g. aircraft engine distributor parts, ignition systems, and so on.

According to McHale,[9] mineral-filled melamine moulding compounds will resist arcing for 135 seconds based on A.S.T.M. tests as against two to four seconds for phenolics. Phenolic resins tend to shrink under heat and arcing conditions. Urea resins stand the arcing but not the temperatures involved.

While having all the colour possibilities of aminoresins it has much higher heat resistance. Its properties seem likely to open up uses for such articles as toaster handles, chafing dishes, electric iron handles, etc.

Chemically, melamine resin has more resistance than the urea resins against weak acids and alkalis, and is also very resistant to organic solvents. In the preparation of mouldings for holding foodstuffs, the resin is particularly to be commended, as it does not react with fruit juices, acetic and citric acids, mustard, fats, and oils. Water absorption of cellulose-filled moulding powder is only 2·7 per cent after 7 days immersion.

The earliest melamine moulding powder was that known as Ultrapas[11] in Germany.

Ultrapas Moulding Powder. This is actually based on an equimolecular resin of melamine and urea.

350	parts formaldehyde
126	parts melamine
60	parts urea
5	parts ammonia (specific gravity 0·9)
1	part active charcoal

It is condensed in a stainless steel kettle fitted with stirrer and jacketed for hot water. It is held at 80° C. for 20 minutes, to a pH of 7. The filtered syrup is added to

160	parts cellulose
1·2	parts zinc stearate
0·25	part magnesium carbonate

Magnesium carbonate acts as a stabiliser preventing pH from dropping below 7.

Batch yield was 380 parts.

Mouldings made from it, in the form of beakers, cups and saucers, etc., were very attractive. In view of the high water resistance of the finished mouldings, the resin has been suggested for the manufacture of domestic utensils. German examples include a bath-tub (presumably for children), a soap-dish, a bath-spray nozzle, and a developing tank for photographic work. All these objects are more or less in continual contact with water or solutions of soap or chemicals in water.

Modification of Melamine Resins. In order that melamine-formaldehyde resins may be used for coatings, they must be compatible with commonly used paint, varnish, and lacquer ingredients, such as solvents, resins, and pigments. To effect this, it is necessary to modify the structure of the condensation unit. As in the case of the urea resins, this is usually done by causing the condensation to take place in the presence of an alcoholic medium. The resulting product is a melamine-formaldehyde etherified product similar in many respects to urea-formaldehyde etherified resins.

As in the case of urea-formaldehyde resins, these condensation products are often further modified by carrying out the reaction in the presence of the ingredients of an alkyd resin and under conditions such that a complex mixed condensate is formed. Perhaps a more common modification, however, is that in which the melamine is mixed with some other substance capable of reacting with formaldehyde in much the same way,—e.g. phenol, urea, and thiourea.

Resins of increased complexity can be readily made by substituting complex or polyhydric alcohols for part or all of the monohydric alcohol.

These hydrocarbon-soluble condensation products are readily converted to hard, water-white, extremely resistant films, by heat or catalysts or both. According to Hodgkin[5] the heat or catalyst functions to release the etherified alcohol and thus makes possible the formation of larger condensation units.

One of the most striking advantages of these condensation products is that, in addition to their hardness, they are extremely heat resistant and remain stable on exposure to temperatures above 260°C., as evidenced by colour retention. Urea-formaldehyde condensations which have a high percentage of carbonyl oxygen are decomposed by temperatures above 180°C. This stability of melamine resin at elevated temperatures, as compared to urea-formaldehyde resins, may be largely attributed to the absence of the carbonyl group.

By a careful choice of catalysts, reaction media, time and temperature, the properties of the solvent-soluble melamine resins may be varied between wide limits. Resins can be made having a low degree of etherification and subsequent low tolerance for hydrocarbon solvents, or they can be made with a high degree of etherification and then have infinite compatability with hydrocarbon solvents such as mineral spirits. Various resins with properties in between the two extremes can be prepared.

Melamine Resins Applied to Coatings. Synthetic resins based on melamine become hard and chemically resistant after they have been heat-treated; consequently, their main application has been for those products which can be baked. Increasing use is being made of varnishes and enamels containing melamine resins. These solutions are being used by most of the techniques employed, in the normal way, e.g. spraying, brushing, dipping and coating generally. The melamine is seldom used as the sole vehicle, but nearly always together with alkyd resins. In this respect they resemble the urea resins. In this country they are made by Beetle Products Co., Ltd., as resins for lacquers and as an additive for urea resin adhesives. In the United States the leading producers are Monsanto, Resinous Products, the Plaskon Corporation, and American Cyanamide.

Melamine resins under the influence of heat set more rapidly than any other thermosetting resin available. In this respect they are far in advance of the urea resins, just in the same way as these were considerably more rapid than the alkyd resins. For example, coatings made with melamine resins attain great hardness after heating for only a few minutes at temperatures of 150° C.

Coatings based on combinations of melamine resin and alkyd resins may be baked to their maximum hardness at temperatures as low as 80–95° C. This is far lower than the range of temperature involved in the use of urea resins. In the ordinary way using urea resins a temperature of at least 120° C. is required in order to give really satisfactory resistance to water. The low temperatures which may be used with melamine resins have extremely important practical implications. It means that ovens heated by hot water or by steam coils may be employed for finishing off products. No special heating equipment is necessary. Clearly this is an outstanding advantage.

In the past it has been a matter of some difficulty to make baking enamels which would retain high gloss and have light colours. Particular difficulty was experienced with white as a colour. Where alkyd resins were employed the coatings when baked,became yellow. Mixtures of urea resins with alkyd resins enabled the production of a satisfactory colour, but on the other hand, after baking, the gloss was affected. Melamine resin is a distinct improvement on these types since high temperature stoving in no way impairs the gloss and colour of the products.

A consequence of the ability to use high temperature for short periods has enabled a considerable speed up in production . This has led to its widespread application for mass produced articles such as refrigerators, switch-boards, motor car bodies, electric irons, metal furniture, bathroom and kitchen ware, etc. Also the excellent resistance to heat which far surpasses urea-formaldehyde has led to their use for stove parts and electrical applications.

Melamine resins are completely compatible with non-drying oils. They are also completely compatible with drying oil-modified resins, and may be employed in proportions varying from 5 to 100 per cent of these. It is a fact that the addition of quite small proportions of melamine resin, for example less than 20 per cent, to an alkyd resin, reduces stoving time by as much as half.

Apart from these factors, melamine coatings have good electrical characteristics, and are non-tracking.

Melamine resins in general have excellent weather resisting characteristics, showing better durability than the urea resins in this respect. They tend to improve the hardness and durability of alkyd resins. A consequence of these desirable features is that they are being employed for outdoor applications generally.

Melamine resins can be prepared which are soluble in organic solvents. To some extent these are being employed in nitro-cellulose lacquers and other coatings. These melamine resins are completely compatible with nitro-cellulose; they are compatible up to 40 per cent with methyl cellulose.

Chemical Resistance. Hodgkin has carried out simple tests in an attempt to compare qualitatively the resistance of melamine-alkyd and urea-alkyd films to various chemicals and water. Immersion tests were made to determine the resistance of melamine and urea resins to concentrated hydrochloric acid, dilute potassium hydroxide, and water, all at room temperature. In each test melamine resin proved superior to urea resin, whether alone or in combination with alkyd resins.

By the introduction of this concentrated melamine-formaldehyde-butanol resin, there are five advantages:

> The baking schedule may be lowered almost 50° C. and still give the hardness formerly secured only with high bakes using alkyd or alkyd-urea-formaldehyde resin enamels alone.
>
> The baking schedule may be speeded up if the same temperature is maintained.
>
> From the standpoint of economy more alkyds can be used with melamine resins than with urea resins and still give the same hardness.
>
> The heat resistance of melamine resins is superior to urea formaldehyde resins; discoloration occurs at 250° C. to the same degree as or to a lesser degree than it does with urea-formaldehyde resins at 150° C.
>
> The chemical resistance appears to be at least equal to the urea-formaldehyde resins, and, in some cases, slightly superior.

The great heat resistance of the melamine resins offers possibilities in the field of flash baking where enamels go through an oven at temperatures of 260–450° C. for very short periods of time.

REFERENCES

1 American Cyanamide Co. U.S.P. 2,199,803; B.P. 549,705/1942; B.P. 556,142/1943.
2 Ciba Company (Basle). Swiss Patent, 193,630/1935. B.P. 468,677/1937.
3 Du Pont and Co. B.P. 583, 504/1946.
4 Henkel & Co. G.P. 647,303/1935.
5 HODGKIN AND HOVEY, HEWETT, BARRATT AND MEISKE. *Ind. Eng. Chem.*, 1941, **33**, 771.
6 I. G. Farbenindustrie. B.P. 458,877/1935.
7 JAYNE. U.S.P. 2,180,295/1939.
8 LIEBIG. Annalen., 1834, **10**, 48.
9 MACHALE. *Mod. Plastics*, 1941, July, p. 39.
10 MACLELLAN. *Ind. Eng. Chem.*, 1940, **32**, 1181.
11 C.I.O.S. XXXIII–23, p. 53.

CHAPTER X

CAST RESINS

THE story of cast resins falls into two sharply defined sections. Until the beginning of the last war cast resins were almost exclusively used for decorative articles and accessories. During the last few years they have come to the fore as accessories to the engineering industries notably for press tools. The simplicity of production and handling have commended cast resins for this very wide field of application. While phenol-formaldehyde resins are still the predominant type, others such as aniline-formaldehyde resin are also used.

Up to the present time urea-formaldehyde resins and melamine resins have not been used on any commercial scale for making articles by casting. Although this was one of the early approaches in respect to urea-formaldehyde resin it has never given satisfactory results.

The moulding process involves a large amount of heavy and expensive press equipment and accessories. High temperatures have to be used, and it has been established that the difficulties in obtaining an adequate range of colours with phenolic resins are in great part due to the high temperatures. By contrast the process of casting eliminates all these disadvantages, although it is not without disadvantages of its own. The process of casting preceded that of moulding, although the commercial development came at a rather later date. Thus by 1904 Story[6] was successfully casting the resins.

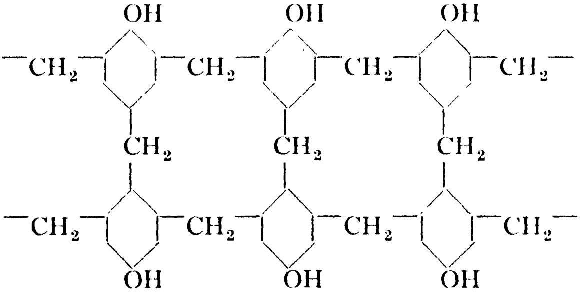
Cast phenol-formaldehyde resins are poured as liquid into a mould just in the same way as molten metal is cast in a foundry. It is then heated in these moulds at low temperatures of between 60–80°C. until eventually the material reaches its insoluble and infusible final condition. The liquid first thickens, then gels, and then progressively hardens. The time necessary to attain maximum hardness is something of the order of several days. This is obviously in sharp contrast to the very short cycle involved in moulding. Resins are now available, the hardening of which can be accelerated to take place in a few hours.

Cast resins were the first means devised to get the full range of colour into phenolic resins. Fillers are not normally used in the same sense as with moulding resins. They are only used to give special decorative effects. As a result it is fairly evident that cast resins must be much more expensive than moulding resins, and this has to some extent limited their use. Latterly fillers have been introduced for products whose appearance is not of great importance.

Preparation of the Resins. Cast phenolic resins were initially made from raw materials much in the same way as the resins for moulding powder were prepared by Baekeland. It was subsequently found that the proportions he used, up to 1·5 mols of formaldehyde for each mol phenol were not the most satisfactory for making cast resins, and could be greatly improved upon. By using 2·5 mols formaldehyde for each mol of phenol, far superior cast resins were obtained. The resins were easier to cast and the final materials could more readily be machined. It was also found that while the condensation was desirably carried out in an alkaline medium, it had to be finished off by neutralising the alkali with a suitable acid. This had the effect of giving products with a much superior fastness to light. The products also had improved flexibility and toughness.

Riesenfeld[5] thinks the increase in the proportion of formaldehyde, as compared with moulding resins, leads to the formation of long chains with corresponding increase in flexibility. He suggested that a definite molecular compound was formed at a proportion of 1 : 2·5 phenol to formaldehyde.

The formula proposed by Megson[4] would appear to fit in well with many of the characteristics and properties of cast resins.



At present, cast phenolic resins are made in the following manner:

Phenol and an excess of formaldehyde are condensed together in an alkaline medium which is subsequently neutralised by means of a suitable weak acid such as lactic acid or citric acid. The excess water is then distilled off under vacuum. It is absolutely necessary to adhere rigidly to the predetermined conditions since the process is very sensitive, and slight variations cause pronounced difference in the finished materials. The manufacturing procedure is carried out in a nickel still which is heated directly with steam. It is fitted with stirring devices and all the control gear necessary for close supervision of the process. The

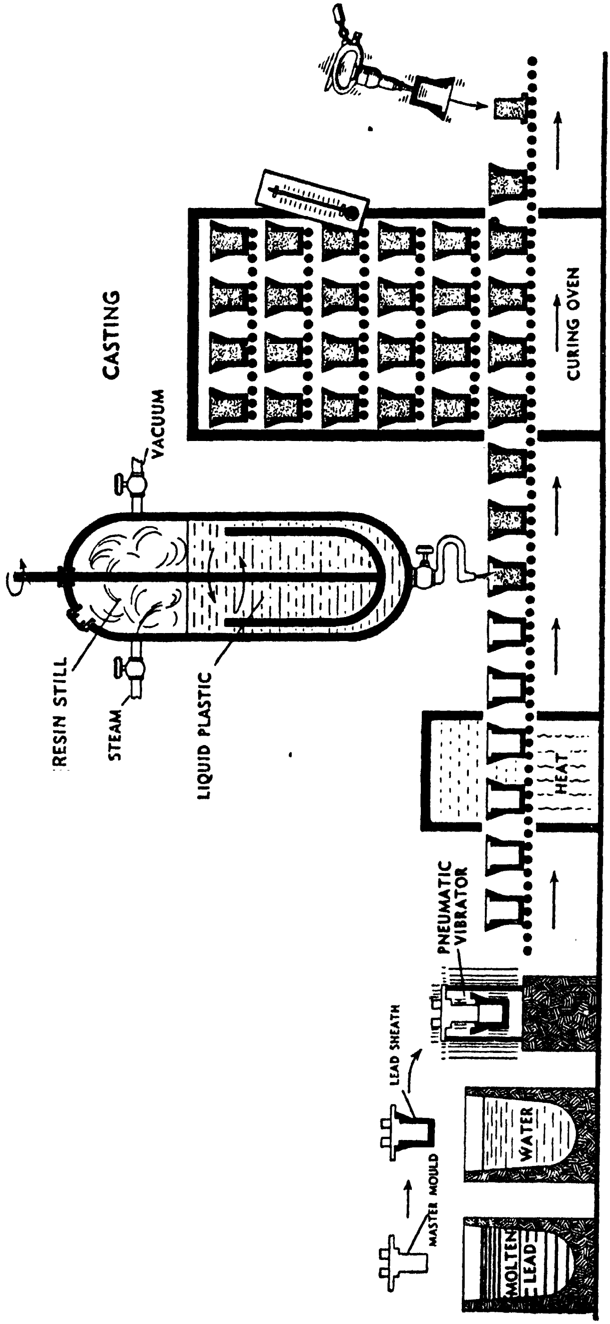


Fig. 88. Diagrammatic representation of the casting method

time of reaction takes some hours. The resin forms and excess water is distilled off under vacuum. Elimination of water is aided by addition of small amounts of glycerine, or triacetin. These, however, have an adverse effect on the properties of the cast resin. Just prior to distillation the requisite amount of lactic acid is added, about 7 parts per 100 parts phenol.

During this procedure the polymerisation of the product is carried forward under the influence of heat. Also, during this distillation period the raw resin, which is a light straw colour, may be dyed by the addition of suitable dyestuffs. Light-coloured cast resins are almost invariably made with pure resins based on phenol.

At one time the resin was stored in this condition before being used. It was liquid when hot, but semi-solid upon cooling. Such resins would be re-melted when required under carefully controlled conditions, then cast in moulds and thereafter hardened by heat.

During recent years knowledge of the properties of these resins has grown. Control of the manufacturing processes has also notably improved, so that now it is possible to cast the resin direct from the production stills, transferring the resin into the moulds without the complication of storage. Excess water has still to be removed by distillation before this is done, and the neutralising acid has to be added. However, this procedure has meant much more rapid production and has led to a lowering of the cost.

PREPARATION OF PHENOLIC CAST RESIN

Phenol (C_6H_5OH)	188 gms.
Formalin (40% H.CHO) . . .	352·5 gms.
Caustic Soda (NaOH) . . .	2·8 gms.

The phenol and formaldehyde are mixed together in a beaker and are poured into a 800-c.c. flask, to which the ground caustic soda is added. This is thoroughly shaken and a condenser attached to the neck of the flask, and the whole heated on a water bath, under reflux for 1¼ hours, shaking the contents from time to time.

The liquor is transferred to a distillation flask, in the neck of which is inserted a glass tube with air-valve and thermometer. The flask is connected to a condenser, and Buchner flask, attached to a vacuum pump. The water is distilled off under vacuum, and the resin is left in the flask. The temperature is kept between 75°–80°C. and if the distillation becomes too vigorous the air-valve can be opened.

(1) If a plasticised resin is required, the requisite amount of glycerine, triacetin, or other suitable plasticiser, is added during the final distillation.

(2) If clarity is a necessary property, the liquor is just acidified with lactic acid after reflux. If an opaque material is required a small amount of water is left behind in the final distillation. This material can be cast and set if left in a thermostatically controlled oven at 70° C. for 4 days.

Loos[3] has described the production of a transparent casting resin. With rapid increase in viscosity of phenol-formaldehyde condensates, difficulty may be experienced in completely eliminating the water of reaction and so obtaining perfectly glass-clear resins. Evaporation in vacuum in admixture with a small percentage of glycerine, triacetin or similar liquid is effective in removing water, but the liquids in question do not improve the physical qualities of the resins. Loos introduced the use of a polymerisation retarder, which is eventually converted into a resin of glass-clear character forming a homogeneous mixture with the phenolic resin. Such an agent is obtained by condensation of acetone with formaldehyde. In themselves the acetone-formaldehyde (or methyl ethyl ketone-formaldehyde) resins have achieved some prominence as industrial casting materials.

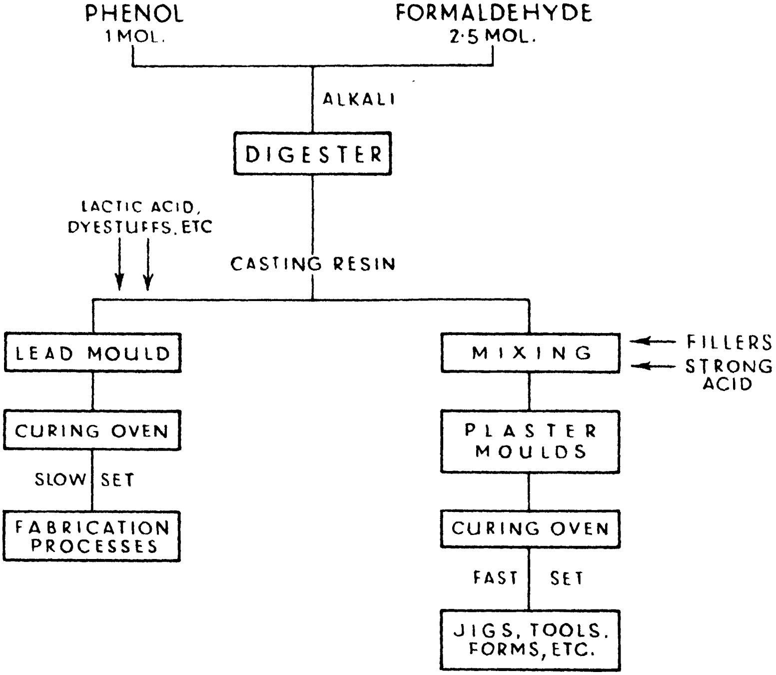


Fig. 89. Flow sheet for phenol-formaldehyde cast resins

In one example the clear hydrosol from 200 parts phenol, 220 parts formaldehyde solution and 8 parts caustic soda (refluxed for 30 minutes) was mixed with the product of condensation of 30 parts acetone and 210 parts formaldehyde solution (this is equivalent to a molecular ratio of 1 to 5) made by boiling for 30 minutes with 6 c.c. normal caustic soda solution. The mixture of the two resins was boiled for a further 25 minutes and then acidified with 30 c.c. 85 per cent lactic acid, after which it was distilled to drive off water and poured into moulds. Cure was effected in five days at 70° to 80° C.

German procedure for making cast resins was along similar lines. The following mixture:

100 parts Phenol (100 per cent pure)
250 parts 30 per cent Formalin
4 parts Caustic Soda

is digested in a nickel still at 65° C. for 3 hours. It is distilled until quite thick (Ostwald viscosity 8).

12·5 parts Lactic Acid

is added and further distillation continues until viscosity reaches 9. The mass is run off into brass trays.

This resin solidifies on cooling. It is melted by immersing in a water bath at 80° C. for 2 hours. It is poured into lead moulds and then cured in ovens for 24 hours at temperature starting at 70° C., rising to 80° C.

Preparation of Moulds for Casting. The production of moulds is a simple matter by comparison with the complex engineering procedure involved in making compression moulds. The moulds for casting resins are usually made by dipping a highly polished steel master die into molten lead and subsequently cooling in water. The lead reproductions of the mould can easily be stripped from the master-core, and faithfully reproduce every characteristic. In this manner any number of lead moulds can be produced very rapidly in a short time. The preparation of the lead moulds has its own technique, such factors as speed of dipping and removal being of great importance. The surface of the mould is a faithful image of the polished surface of the steel master mould. This imparts a smooth surface to the resinous castings. The polish is not as high as that on the steel mould surface. However, cast resins have the useful property of easily acquiring an exceptionally brilliant lustre and polish. Simple polishing confers additional values in gloss and patina. The maximum gloss is obtained by casting in a glass mould or in highly polished or plated moulds.

The process is extremely economical; each lead mould is used only once, thereafter being re-melted for conversion into another mould. The only loss of material is caused by the formation of a small quantity of lead dross. It is necessary that the moulds should taper slightly to facilitate the removal of the castings.

When the lead mould has been filled with the resin either by hand or direct from the still, it is placed in an oven for heating. The temperature of such ovens is carefully maintained at the desired value by circulating hot air and they are thermostatically controlled. In the normal way temperatures ranging between 60° and 80° C. are employed. The time of cure will depend upon the nature of the resin employed and normally ranges between 3–8 days. The optimum hardness of test samples is the criterion of the final product.

The set castings are ejected from the mould by means of pneumatic hammers worked by compressed air. The castings may be knocked out while hot, and are ready for fabrication. Castings several feet long may be made in this way. Almost any cross-section may be made. Numerous articles can be fabricated by the simple procedure of slicing these lengths. This procedure is adopted in the production of such articles as buttons, buckles, clock cases, even radio cabinets, and of course a host of decorative articles.

A variety of decorative effects may be obtained by the incorporation of other coloured cast resins during pouring. The method of mixing is important if reproducible results are to be obtained, and conditions once established, must be strictly adhered to. The general appearance of the finished article depends to a great extent on this. By the introduction of metallic particles or other decorative fillers a wide variety of unusual effects is secured.

Properties of Cast Resins. Cast resins have a number of outstanding characteristics which make them highly valued. For one thing they are available in an unlimited range of colours, and different effects, transparent, translucent, mottled, etc. They are non-inflammable and extremely rigid. They have excellent properties, the tensile strength and impact strength being extremely high. Suitably finished, they have a remarkable gloss and patina which is extremely attractive. From the point of view of fabrication the ease with which they can be machined is one of the outstanding attributes.

The cast resin possesses the interesting and useful property that it is very slightly thermo-plastic. It can be distorted by heat above temperature of 50–80° C. and it withstands temperature up to 80° C. almost indefinitely. It can be slightly softened by immersion in hot water for a few minutes and is then fairly flexible. In this form it can be bent to a limited extent and formed. After being bent, it is immediately cooled by immersion in cold water, and retains the new shape. Straight rods can be bent into a variety of shapes in this manner.

Cast resins are unaffected by immersion in cold water. Thus after 24 hours immersion the water take-up is of the order of 0·4 to 0·7 per cent. They are only slightly affected by weak acids or weak alkalis. They are decomposed by strong acids or alkalis. They are insoluble in alcohols, ketones, esters, aromatic hydrocarbons such as benzene, aliphatic hydrocarbons, and so on. They are not influenced or affected by mineral oils, animal oils, vegetable oils, greases, etc. They harden slightly with age. The only effect of sunlight or ultraviolet light is a slight yellowing.

TABLE 57

MECHANICAL PROPERTIES OF CAST PHENOLIC RESINS

Specific gravity	1·30–1·335
Refractive Index n_D	1·66
Tensile strength, lb./sq. in.	5,000–11,000
Modulus of Elasticity, lb./sq. in. by 105	3–18
Impact Strength, Izod (notched)	0·2–1·25
Brinell Hardness, 25 kg. load	30–45
Compression Strength, lb./sq. in.	25,000–30,000
Shrinkage	Up to 1%

Cast resins may be employed to make awkwardly shaped articles with under-cuts which cannot be made by the foregoing procedure. In these instances glass moulds are employed. For example, products such as billiard balls and fancy handles are made in this manner. In each instance the glass mould is destroyed to release the casting. Another method for preparing complicated shapes such as sculptured articles, statuettes, etc., makes use of rubber moulds containing collapsible cores. A comparatively recent procedure has come into use using split moulds for the production of products which more closely resemble compression moulded articles.

Transparent water-clear material can be produced, having a light transmission of about 80 to 90 per cent, and a refractive index n_D 1·66, higher than ordinary glass. Starting from an almost colourless basic material, the colours marketed comprise the full range of almost all known shades and tints, including plain and mottled tints.

The colours are almost without limit, and so are the shapes. Standard sheets, rods, tubes, all kinds of special shapes similar to metal castings, are available ready for immediate use. Door, window and furniture handles and fittings of all kinds are sawn from profile castings.

Pen-holders, inkstands, bracelets, serviette rings, ash-trays, motor-car fittings and (rather important) buttons and buckles, and so on, are made in a similar way. All these castings can be converted into finished goods by the use of standard manufacturing equipment.

Cast resins have fairly good electrical characteristics and have some use for decorative, coloured applications.

The extra toughness and flexibility of cast resins is shown in their behaviour in turning operations. They give long continuous shavings such as are not usually obtained with moulded materials.

TABLE 58

ELECTRICAL PROPERTIES

Volume Resistivity, ohms/cms.	Up to 10^{14}
Breakdown Voltage, 50 cycles, volts/mil.	250–400
Dielectric Constant, 50 cycles	4·5–7·5
10^6 cycles	5·0–7·5
Power Factor, 60 cycles	0·01–·02
10^3 cycles	0·005–0·08
10^6 cycles	0·01–0·045

Handling of Cast Resins. Cast resins may be carved, engraved or embossed in the same manner as ivory, bone or wood, either by hand or by suitable machinery. Excellent carving of very small designs can be produced by the use of abrasive discs or small milling cutters such as used in the dental industry.

For sanding and grinding, the same equipment as for work with brass or wood may be used; for polishing, standard polishing compounds may be applied on ordinary mops or buffing wheels made of muslin discs. The very excellent results and the uniform high gloss so obtained make this material outstanding among the plastic materials available on the present market.

A very successful polish, important for mass production, can be effected by means of the tumbling barrel method, which gives a highly glossy surface.

An interesting application is their use for domestic purposes, as knife handles, knobs for kitchen utensils and similar applications. They have no odour or taste, and are quite non-toxic. They need not be cemented on to the metal parts. A hole slightly smaller then the part to which the handle is to be fastened is first drilled; the handle is slightly softened in hot water and then shrunk on to the metal part. This gives an absolutely tight fit, which will be not affected by subsequent application of heat.

Although the resins are non-porous, it is possible to colour the surfaces in a manner similar to that used for casein and like materials. The material is immersed in a warm solution of the dye until the desired shade has been attained. The dye solutions do not penetrate into the material to a great extent, though they are stable, and cannot be washed off.

Sheets are made from cast resins. Previously they were made by the wasteful procedure of cutting them on band saws from cast and fully hardened blocks.

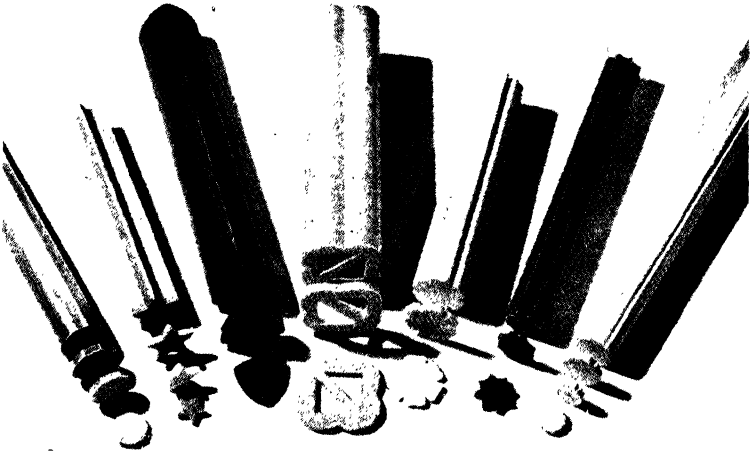


Fig. 90. Cast resin rods for buttons and tubes for buckles with blanks sliced off for making finished buttons and buckles[9]

It was then realised that a block of resin could be cast and hardened only to about two-thirds of its final hardness, then taken out of the oven and put on to a sheet-cutting machine while still warm. Such a machine is similar to the planing machines used in the celluloid industry (*v.i.*) where the block is fixed on a movable table, which feeds it against a stationary cutting knife. The block is cut into sheets of any desired thickness. The sheets are then returned to the hardening ovens, where they remain until they attain their final hardness.

Another interesting application of the above technique which has led to considerable saving of material is in the manufacture of buttons, buckles, and all sorts of similar shapes from cast resins. Previously these articles were sawn out of sheets, a slow process accompanied by waste of material.

Preparation of Buttons and Buckles. Recently, methods and specially designed machinery have been developed whereby hardened profile rods for buttons (round, square, hexagonal, scalloped, and so on), as well as buckles and all sorts of sundry shapes may be heated up in water, or preferably in a mixture of water and glycerine, until after a short time they reach the degree of softness necessary for the process. They are then sliced like cheese in a shearing machine. This consists of a knife which moves horizontally against a stationary die. This is heated to keep the profile castings warm and plastic. They are automatically fed against the knife, and sliced into the desired thicknesses without any waste.

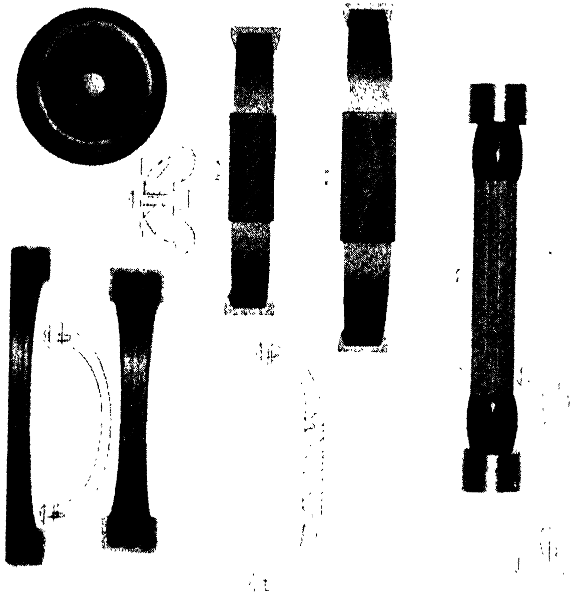


Fig. 91. Door handles fabricated in cast resin[9]

The rate of cut is very rapid, ranging between 800 and 1,200 blanks per hour, depending upon size, shape, thickness, etc. The blanks obtained in this way are almost free from tool marks. The blanks are then treated on automatic forming and bending machines which simultaneously punch holes into them. They attain their final polish in a tumbling machine. This type of cast phenolic resins has been widely used for the manufacture of buttons.

The Widening Field of Application. Until comparatively recently cast resins were only employed for making comparatively expensive articles used for decorative purposes. This was due to the excellent colours and brilliance of the products. Latterly, however, there has been a strong trend to use them for more strenuous engineering purposes. This has been so successful that cast resins have already attained outstanding importance in the production of jigs and tools, notably in the aircraft industry. It has been found possible to add fillers to cast resins, which enhance the physical strength characteristics particularly in their capacity to withstand compressive stress. Fillers used include wood flour, shredded fabric, ground phenolic mouldings, and in the United States ground walnut shells. Up to 40 per cent of fillers may be used. The use of these fillers to a great extent offsets shrinking tendencies. Straight resins in the ordinary way shrink about 0·0008 inches per inch from 80° C.

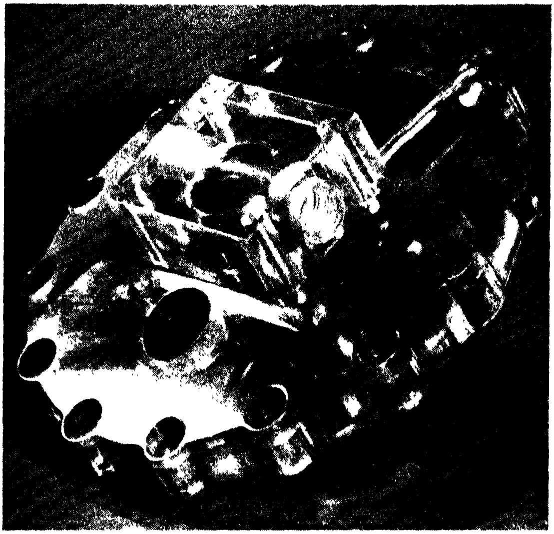


Fig. 92. Transparent cast resins used for demonstration purposes

The casting of synthetic resins along the lines already described is a fairly lengthy procedure. The point here is that in order to get transparency and brilliant colour effect it is necessary to set the resin at low temperature, which takes a long time. Since colour is of no importance for technical applications the setting can be effected much more rapidly by accelerated methods, using strong acid setting agents. For example, 2 hours at 80° C. is a typical cycle employed in making industrial castings.

The leading materials used here are those known as "Catacol"[1] and "Catafil." One of the early materials in this field was the German Dekorit. This was a fully hardened cast phenolic resin with superior mechanical characteristics. It could be machined and was fairly widely used in many applications, notably in the chemical industry, as substitutes for special alloys and ebonite.

Earlier forms of production in the United States included phenolic guide shoes used in oil drilling equipment, cast gear wheels, casting boxes for making other phenolic castings, and so on. But the outstanding feature has been their use as sheet metal forming dies. They have been successfully used for forming steel, aluminium, and so on.

Experience has shown the following outstanding features:

1. Plastics may be substituted for steel and dural in many cases.
2. Tools may be cast to a massed part or placed mould more quickly than by machining or moulding or hand-fitting.
3. Duplicate tools may be economically and quickly made for transport to other plants.
4. Duplicate tools may be fabricated at lower cost than the original owing to the fact that moulds are saved.

In this field of activity the lightness of cast resin as compared with metals is of the utmost importance. For example, zinc forms are seven times as heavy as typical plastic forms.

This tends to increase production by reducing labour requirements since they are so much lighter than metal forming blocks. There is no limitation on the size of the casting. Thus in one operation concerned with the production of Mosquito aircraft a solid cast die, 15 ft. long, is employed.

The trend for the use of cast resins in this way has become very marked both in the United States and in this country. Large numbers of tools are made of cast resins used both for drill jigs and for forming dies. Their strength is shown by the fact that they are able to stand up to a pressure of 4 tons per square inch in hydraulic presses.

At first, plastics were accepted rather unwillingly in this field of manufacture, but this attitude has now changed. Plastic tools are widely employed in many aircraft establishments.

The reasons for this rapid transformation are that the usual methods of drill jig construction, using wood with inserted metal bushings, have certain disadvantages:

1. It is necessary to create three-dimensional contours in wood. This is largely manual, hence slow and expensive.

2. Bushings need often to be retained by steel nests or straps. This adds many complications.
3. Wood is affected by moisture and oils and needs constant maintenance.

The requirements of satisfactory thermo-plastics such as are used may be summarised as follows:

a. The ability to cast the material between 100° and 180°C. so that the jig may be cased in an aluminium alloy part without damaging the latter.
b. A softening point of not less than 90°C. so that it will not soften by frictional heat during drilling.
c. The desirability for shrinkage control during moulding.
d. Ability to finish off with standard wood-working tools.
e. Impact strength adequate to withstand shocks of handling.
f. Absence of brittleness at low temperature or on ageing.
g. Resistance to lubricating oils and metal chips formed in drilling.

It has been found that casting plastics are applicable to drill jigs, formed router blocks, shaper blocks, saw jigs, checking fixtures, hydro form blocks, dies, punch jigs, forming dies for Perspex. In short, most jigs that involve contours.

Apart from replacing materials in short supply there is no advantage in using cast resins where no contour is involved.

Different Types of Plastics are used for Casting. Several different types of cast resins are employed in making engineering products. One type is based on normal thermosetting cast resins which are caused to set very rapidly by the addition of an acid accelerator. The other types are based on the use of thermoplastic materials which give satisfactory performance in the required range of temperature. Several materials have been used in this second type, the outstanding one being a phenol-acetone plastic, and an ethyl cellulose composition has also come into use.

A great deal of information has been made available of the methods used by the Lockheed[2] and Vega Aircraft Companies.[8] Somewhat similar processes are carried out on a very large scale by aircraft companies in Great Britain.

The most generally practised procedure is the use of a phenol-formaldehyde resin with an accelerator. The phenol-formaldehyde resin used for this type of work is a syrup of comparatively low viscosity and is thoroughly mixed with a liquid catalyst before a filler is added. The catalyst is a strong acid. This form is very suitable for casting and is easy to handle. The mixture is then poured into the mould. This may be of plaster of Paris, wood, glass, rubber, metal or other materials. The plastic is thoroughly hardened after it has been baked for 2 to 12 hours at about 80°C. It shrinks slightly on cooling and may easily be removed from the mould. Little or no finishing is necessary.

The ratio of phenol to formaldehyde is different from that in the ordinary cast phenolics. An external catalyst is added at the time the plastic is to be used. Fillers are usually used in the liquid phenolic resins. Substituted phenols such as cresol may be used in place of phenol.

As has already been implied, the liquid phenolic casting resins are thermosetting phenol-formaldehyde resins that are stable at ordinary temperatures until accelerator or setting agent has been added after which they have a limited life.

The mould is filled cold and the resin is caused to set by being baked. Very modest equipment may be used. The thermosetting composition is prepared in an ordinary dough mixer. In this the resin together with fillers and the catalyst are thoroughly mixed. It is essential to achieve good mixing, otherwise uneven products are obtained. The material is thereafter poured into the mould and baked at 80°C. in an ordinary oven. Simple moulds may be used constructed of plaster, wood, etc., suitably protected against attack from the acid used to set the resin. Obviously if the mould is of a porous material it must be sealed by means of a lacquer.

In general, excess plastic is poured into the mould, and allowed to stand for at least half an hour, so that air bubbles may rise to the surface. The baking procedure used depends upon the size of casting; for example, castings up to 1 gallon take 2 hours at 80°C., castings up to 4 gallons take 3½ hours, castings up to 12 gallons take something like 8 hours. It is absolutely essential that castings made by this method must be fully cured.

The alternative phenol-acetone resin was developed to fulfil the requirements of aircraft production. It is a phenol-ketone condensation product produced by reacting phenol and acetone in the presence of an acid catalyst to form a fusible thermoplastic resin which will not set. It is extremely tough, and has a compression strength of about 3 tons per sq. inch. Its deformation temperature is 80° C. and it shows no tendency for cold flow at ordinary temperatures. The procedure adopted with this material is to raise it to 140° C., and pour it into the mould.

The material based on ethyl cellulose, known as "Thermocast",[7] is a recent development. This takes advantage of the extremely high heat stability of ethyl cellulose. Ethyl cellulose is suitably compounded with fillers, pigments, etc. It is heated until it becomes fluid, and is then poured into a mould, becoming rigid when cooled.

The equipment required in this process is extremely simple; thus, Lockheed prepare their material in a jacketed kettle equipped with an agitator. At Vega, they prepare the thermosetting composition in an ordinary baker's bread-mixer, and the job is finally baked at 80° C. in ordinary ovens. Vega use such castings as punches in place of lead.

Naturally full consideration and discretion must be used to determine whether these techniques are applicable for the particular job.

The most widely used material is phenol-formaldehyde resin plus an acid catalyst to speed up the setting time. Although the emphasis here has been on the mechanical properties the material has good electrical characteristics and has great possibilities for electrical applications. There are many possible applications in the electrical field as insulating and supporting materials. For example, there are possibilities in joint boxes, etc.

REFERENCES

1 Catacol. Technical Literature of Catalin, Ltd.
2 Lockheed Aircraft Corp. *Machinery*, Sept. 10th, 1942, p. 1.
3 Loos. U.S.P. 2,206,006.
4 Megson. *Trans.* Faraday Soc., 1936, **32**, 336.
5 Riesenfeld. *Trans. I.P.I.*, 1939, **11**, 25.
6 Story. *J.S.C.I.*, 1906, **25**, 195.
7 Thermocast. *British Plastics*, 1943, **15**.
8 Vega Aircraft Corp. *Machinery*, Sept. 10th, 1941, p. 1.
9 Photographs by courtesy of Catalin, Ltd.

CHAPTER XI

LAMINATED MATERIALS

NEARLY all plastic materials may be used as bonding agents for preparing laminated materials. In a sense this is merely the use of a continuous length of filling material rather than the finely divided forms employed for moulding powders. The behaviour of the products will depend on the nature of the binder. If thermoplastic, then the flow characteristics of the plastic will become evident as the temperature is raised. The best known types are based on thermosetting resins.

One of the most important fields of application of phenolic resins in particular is in the production of laminated materials. The idea is not novel for it had been long practised with materials such as shellac, but the products with synthetic resins have many really superior properties. The principle here is that layers of paper or fabric or other woven materials are impregnated with a solution of phenol-formaldehyde resin. The layers are superimposed and then subjected to heat and pressure. In this way they are compacted to a dense, solid, uniform material which for many purposes is far superior to the moulded or cast forms of phenolic resin. Materials have been evolved which not only have exceptionally good mechanical and electrical properties but which may have pleasing surface finishes, thus extending their scope to decorative and ornamental purposes.

In practice the impregnated sheets, which are first freed from solvent, are piled in layers up to the height which is determined by the thickness of the desired finished product. The pile is then subjected to heat and pressure under the same conditions as used for moulding. In effect, what happens then is that the resin first fuses, becoming liquid and impregnates the sheets thoroughly, finally setting them into a compact, tough, uniform unit. The final material no longer has any resemblance to layers of paper or fabric. The mass of paper or fabric has been transformed by the moulding process and can no longer be re-softened by heat. The mass is non-hygroscopic, and has acquired considerable mechanical strength. It also has very good electrical properties. By rolling impregnated paper or fabric around steel mandrels and placing these in moulds, simple forms of laminated material, such as tubes and rods, may be manufactured.

The Impregnating Process. This may be carried out by several methods. First, the paper or fabric may be immersed in the solution of the varnish. The solution is usually a one-stage thermosetting phenolic resin taken up in alcohol. In this case it picks up a quantity which may be adjusted by running between squeeze rolls. In the second case, the paper or fabric may be coated on one side, any excess material being scraped off by a knife. The other method involves indirect application of varnish, which is picked up by an intermediate roller and applied to the paper or fabric.

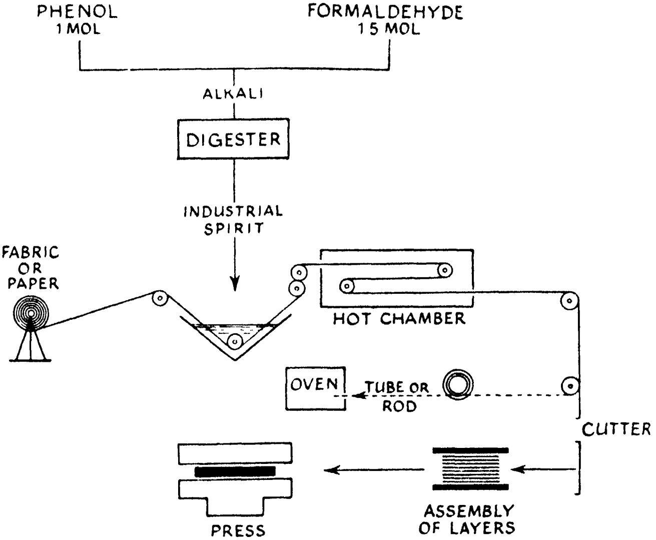


Fig. 93. Flow sheet for making laminated products

The actual choice of method will depend entirely on the desired content of resin, and this may be between 20–80 per cent of the total weight depending on the application for which it is intended. In order to build up a heavy coating of resin, where required, the sheet may be run through the impregnating bath twice, or as many times as may be necessary. In general, high resin contents confer better electrical characteristics. Paper or fabric with a heavy resin coating on one side is frequently used for the preparation of surface coatings. In such an instance the core would be composed of straightforward impregnated material.

The Drying Process. The impregnated material containing resin with a large amount of solvent is dried by passing through a steam chamber which is heated either by steam coils or by hot air. In this way excess solvent, usually alcohol, is driven off and may be recovered in a solvent-recovery plant.

Where laminated sheet is being prepared, then the continuous impregnated sheet is cut to size and the requisite number of layers is assembled on highly polished metal plate. The number of layers employed will depend on the final thickness required, which may be as much as six inches. In the normal way when laminated fabric is being prepared the same fabric is used throughout the thickness. In the case of laminated paper this may be either used exclusively, or the procedure already outlined may be adopted of superimposing specially treated surface sheets. The point about using different surface sheets is that a surface layer having special characteristics may be obtained. For example, a surface layer of high resin content will yield high surface electrical characteristics which may be extremely desirable. Alternatively a flexible soft surface sheet may be admirably suited for embossing any desired surface design. Another possibility is the production of decorative and coloured materials having a printed or coloured sheet serving as the surface unit. Such decorative finishes may also be inlaid into the surface layer. Many such decorative surface sheets are based on papers impregnated with urea or melamine resins.

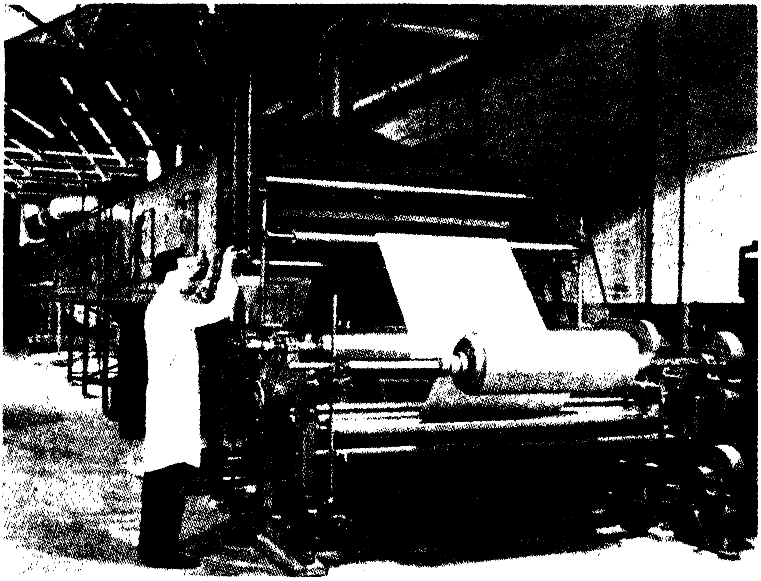


Fig. 94. The impregnating process[11]

Pressing Laminated Sheet. Laminated sheet is usually pressed in large presses having numerous platens, the platens having large surface area. It is customary to use highly polished metal plates having an extremely hard surface. The finished material will faithfully reproduce the surface of these plates. It is quite usual to employ stainless steel for the purpose.

It is also common practice to have assemblies of several packs of sheets for pressing in the same aperture of the press. This illustrates that the output of a large press will be considerable. The heating conditions obviously must depend on the nature of the phenolic resin employed and also the purpose for which the material has to be applied. In the normal way temperatures between 125°C. and 160°C. are generally used. The pressure used is of the order of $\frac{3}{4}$ ton per sq. inch. The time of treatment depends almost entirely on the thickness of the laminated product. It may range from forty-five minutes in the case of a fairly thin product up to six hours for some of the really heavy laminated slabs. The passage of heat through a mass of material is comparatively slow. Furthermore it is essential to cool the material prior to bringing it out of the press, otherwise it will tend to buckle. Recently new methods of heating by means of high-frequency power have greatly reduced the time of heating and give much improved products.

It is desirable that complete setting of the resin should be attained, otherwise many characteristics, particularly resistance to water, solvents, and corrosive agents are adversely affected.

Materials Employed for Making Laminated Products. Almost all materials which are available as continuous sheets have been used in the preparation of laminated products. Most types of paper are used on a commercial scale. These range from pure rag paper, which is the strongest and best, down to the kraft type of paper which is, of course, also characterised by high tensile strength. The particular variety of paper employed will depend almost entirely on the requirements. The characteristics involved are colour, finish, degree of impregnation, and so on.

In the same way almost every type of fabric is employed, ranging from very lightweight fabrics up to the really heavy ducks, canvas, and so on. For the average run of industrial purposes light- and medium-weight fabrics are generally used. These cover the types which weigh between 3 to 16 oz. per sq. yard. However, for the production of really heavy-duty materials which are employed for gears, bearings, etc., heavy sheetings which may weigh up to 40 oz. per sq. yard are utilised as the basis of the laminated product.

Brown[4] has described the effects of different materials employed making laminated sheetings.

(1) *Paper.* Many kinds of paper are used, including manila, sulphite, kraft, alpha-cellulose, and cotton paper, and according to the use to which the final product is to be put, papers vary from relatively hard, well-beaten papers to soft and highly absorbent papers. The physical characteristics of the paper must be uniform; in particular any variation in thickness or absorbency will lead to inconsistency in the resulting products. The paper must be chemically neutral, a pH value of 7 to 8 being commonly specified. If a non-porous type of paper is required, this property must be obtained by highly hydrating the paper fibres in the beating engine and not by any chemical process of parchmentising. The absorbency of the paper filler controls the proportion of synthetic resin in the final product. A highly porous paper will absorb a high percentage of resin, whilst a hard, non-porous paper will absorb but little. The effect on the characteristics of the laminated product by varying the resin content will be discussed later in the paper.

(2) *Fabric.* Fabrics of American cotton, Egyptian cotton and linen are commonly used, whilst jute, silk, artificial silk, glass fibre, and asbestos find application for certain purposes. Cotton fabrics vary from light cambric to heavy duck cloths; generally plain square weaves are used, but moleskin, corded fabric, and other special weaves may be required.

Laminated plastics manufactured from woven fabric are rarely so strong in tension as those made from paper. This is due to the crimp in the thread caused by the crossing of the warps and weft. When a laminated fabric plastics is stressed, the full reinforcing effect of the cloth is not secured until the material has become sufficiently elongated to pull the longitudinal threads as straight as the interlocking construction of the cloth will permit. With ordinary square weaves considerable elongation is required, and usually before this can be effected the synthetic resin in which the fabric is embedded will fracture. Considerable thought is given to the design of fabrics intended for laminated plastics, in order that this effect may be minimised. In order to produce really high tensile sheets, special cord fabrics have been manufactured in which the weft threads are held perfectly straight without crimping. These wefts take the form of cords held together by much lighter warp threads. The resulting plastic has exceptionally high tensile strength in the direction in which the cords run, but a low tensile strength in a direction normal to the cords. Laminated fabric plastics have a high resistance to shock loads.

(3) *Synthetic Resin.* Phenolic resins are most commonly used for laminated materials, although aniline and urea resins are also used. Some thermoplastics have found an application in certain electrical insulation materials.

Of the phenolic resins, those synthesised from cresylic acid produce material having low dielectric losses, whilst resin synthesised from phenol confers greater mechanical strength. The type of catalyst used has an important influence on the resulting plastics, caustic soda being suitable for the production of high mechanical strength resins, but being quite unsuitable for electrical products, due to its deleterious effect upon the power factor, particularly in the presence of moisture.

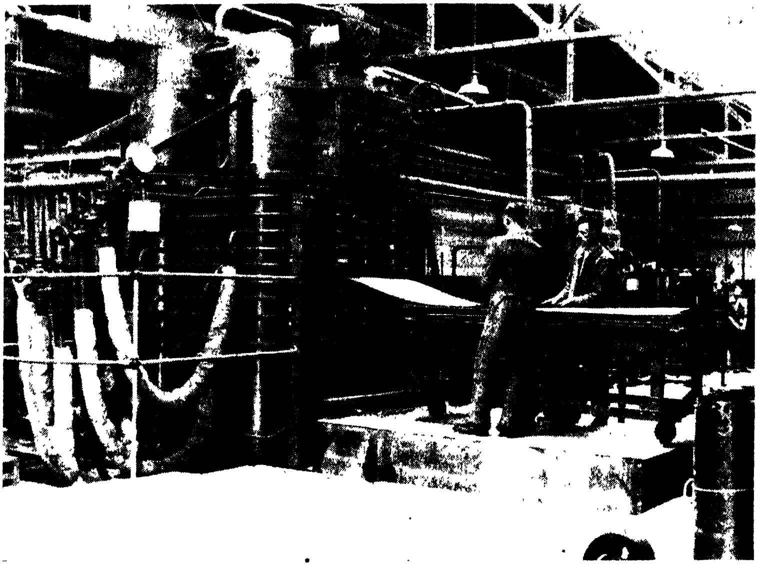


Fig. 95. Removing sheets of laminating material for the press[11]

The resin may be dissolved in alcohol to form a varnish, or a portion of the alcohol may be replaced by water.

In the search for materials which will give even higher tensile strength and impact strength, cords have also been applied. This follows the example of tyre carcasses where cords are found to give the best service. Various proprietary types of laminated products are manufactured on the basis of cords made from cotton, linen, rayon, etc.

Latterly there has been a trend to use plastic fibres for weaving into fabrics which are then laminated in the usual way. Nylon and polyvinylidene chloride are two examples.

Other materials which can be formed into continuous lengths are also used. For example, woven asbestos is employed for products where heat resistance is the major consideration. In such instances it is used together with a special heat-resisting resin. Woven glass fabrics have also been used for laminated sheets and have found their mai application for electrical purposes.

It is clear that in the case of paper or fabric, the resin impregnate and bonds the materials. With asbestos, glass, etc., the action i merely bonding. It is claimed at the present time that continuou filament glass cloth impregnated in this way has tensile strength up t 60,000 lb. per square inch.

TABLE 59

STRENGTHS OF FABRIC BASE LAMINATED SHEET[6]

Material	Tensile, tons per sq. in. 0°	Tensile, tons per sq. in. 90°	Tensile, tons per sq. in. Prolonged Loading, 0°	Compression, tons per sq. in.	Shear, tons per sq. in.	Young's Modulus, 0° lb. × 10⁶	Shear Modulus lb. × 10⁶
High-grade cotton fabric (uncrossed)	9·55	6·85	7·10	9·80	3·15	1·46	0·45
Cotton fabric (crossed)	8·12	7·74	6·66	9·60	3·15	1·38	0·33
Low-grade cotton fabric	6·47	7·10	4·70	8·86	2·56	0·97	0·33
Cotton fabric	6·40	6·74	4·68	9·89	3·10	1·08	0·31
Cotton fabric	5·04	5·33	3·85	11·52	2·56	0·90	0·34

It should be realised that the strength and toughness of pressed laminates depend on both the resin and the filler. Each will play its part. Acid resins should be avoided because they tend to make cellulose tender. Some thermosetting resins, when used to produce glass cloth laminates, produce excellent strength characteristics, yet the same resins may be quite unsuitable for cloth or paper-base laminates.

Consideration so far has been confined to phenol-formaldehyde resins. As already mentioned other plastic binders may be used. Urea and thiourea formaldehyde resins are employed to produce attractive laminated products. In particular, paper or fabric impregnated with such resins are extensively used as surface layers over cores of phenolic resin impregnated materials. In this way surfaces in pastel shades of every description may be attained. Thus laminated material based on paper with such a special white surface has been extensively used for refrigerators. By using urea resins throughout, translucent or light-coloured laminates are obtained by use of suitable paper or fabric. In this instance the paper or fabric is impregnated with urea-formaldehyde syrup or solution and is then dried out at about 90° C. There is no question of using solvents. Products based on urea resins will have the

TABLE 60

PROPERTIES OF TYPICAL LAMINATED MATERIALS[1]

Physical Properties	Typical high-grade paper laminated for h.t. insulation	Typical type of ordinary grade paper laminated for l.t. insulation and mechanical purpose	Special grade of paper laminated for tropical uses and h.f. insulation	Standard type of fabric laminated material for gears and mechanical uses as specified in B.S.S. 668	Standard type of fabric laminated material having high mechanical strength
Ultimate tensile stress (lb./sq. in.)	13,000–15,000	15,000–19,000	7,800–9,200	8,500–11,000	13,000–15,000
Shearing stress (lb./sq. in.)	10,000–12,000	15,000–17,000	9,000–11,000	11,000–13,000	14,000–17,000
Percentage yield under 10,000 lb./sq. in. compression	1·2–1·8	1·0–1·6	1·0–1·5	2·0–2·5	2·6–3·6
Specific gravity	1·31	1·38	1·33	1·34	1·34
Coefficient of expansion per °C. through laminae	·00005–·00009	·00013–·00017	·00003–·00005	·00007–·00011	·00008–·00011
Volume resistivity (megohms/cm.^{3})	10^7–10^8	10^6–10^7	10^8	10^3–10^4	10^3–10^4
Surface resistivity (megohms/cm.^{2})	10^6–10^7	10^5–10^6	10^7	10^2–10^3	10^2–10^3
Power factor at 800 cycles (%)	1·5–3·5	2·5–4	1·5–2·5	20–40	20–40
Dielectric strength at 90°C. (volts/mil.)	200–400	120–200	300–600	30–60	30–60
Dielectric strength at 20°C. (volts/mil.)	400–600	350–450	400–700	80–120	80–120
Breakdown along laminae at 90°C.	30–40 K.V.	20–30 K.V.	70–100 K.V.	5–7 K.V.	5–7 K.V.
Dielectric constant	5·4–5·7	5·7–6·3	4·2–4·5	9–11	9–11
MOISTURE ABSORPTION					
$\frac{1}{32}$" thickness	0·90%	3·5%	0·25%	—	—
$\frac{1}{16}$" thickness	0·60%	2·1%	0·15%	$\frac{1}{4}$" ·50%	$\frac{1}{4}$" ·50%
$\frac{1}{8}$" thickness	0·40%	1·1%	0·09%	$\frac{1}{2}$" ·45%	$\frac{1}{2}$" ·45%
$\frac{1}{4}$" thickness	0·25%	·40%	0·06%	—	—

usual limitations such as low heat resistance. Melamine resins are also employed. They give excellent transparent effects, and have high heat resistance.

The use of other impregnating materials in the thermoplastic field have limited application because they are thermoplastic and flow under heat.

Paper, fabric, etc., are not the only base materials used. Fibres, either as cords or aligned, have been employed and have given materials having remarkable physical properties.

De Bruyne[2] has had great success in this field. The earliest of these materials was known as "Cord", material which had a tensile strength of 25,000 lb. per sq. inch, depending for this figure on the use of a special type of cotton reinforcement. The substitution of linen reinforcement for the cotton formerly employed, and the use of a special technique or orientation of the fibres before impregnation, led to the production of a material known as Gordon Aerolite, with the astonishing tensile strength of 45,000 lb. per sq. inch or four-fifths of that of duralumin, and a density of only half that of the alloy.

The fibres are oriented or aligned in a special machine and passed on a band without disturbance of the orientation through the impregnating bath, after which the impregnated slab is dried. It passes to a trough or mould 30 ft. long which is placed in a 800 ton hydraulic press and emerges as a board 6 in. wide and 30 ft. long of any required thickness, and possessing outstanding physical properties. Recently, oriented cotton fibres have been found to give even more impressive results.

Preparation of Tubes and Rods. In addition to the large-scale manufacture of sheet materials production of laminated tubes and rods is also very important. Tubing is made by a simple procedure. Impregnated paper or fabric is wrapped over a metal mandrel. This may be baked in an oven, thereby setting the resin, and a tube is thus obtained. Much stronger products can, however, be obtained by submitting the tube to pressure while it is being heated. This is carried out by placing the tube in a split mould so that pressure may be applied. Extremely large tubes ranging up to several feet in diameter are prepared in this manner.

The preparation of rod is carried out by rolling the impregnated material on to a very small mandrel or wire. When the desired thickness has been built up the mandrel is removed. The roll is then placed between split moulds and is heated under pressure giving a solid rod.

Tubes and rods are subsequently ground to exact diameters. It is usual to finish them off by buffing, or alternatively by coating them with a varnish.

Laminated materials of this type have been used to a limited extent for the production of simple moulded shapes. This procedure is particularly favoured if the laminates are not quite fully cured. Articles such as small gears, pulleys and even trays can be made by direct moulding of laminated assemblies.

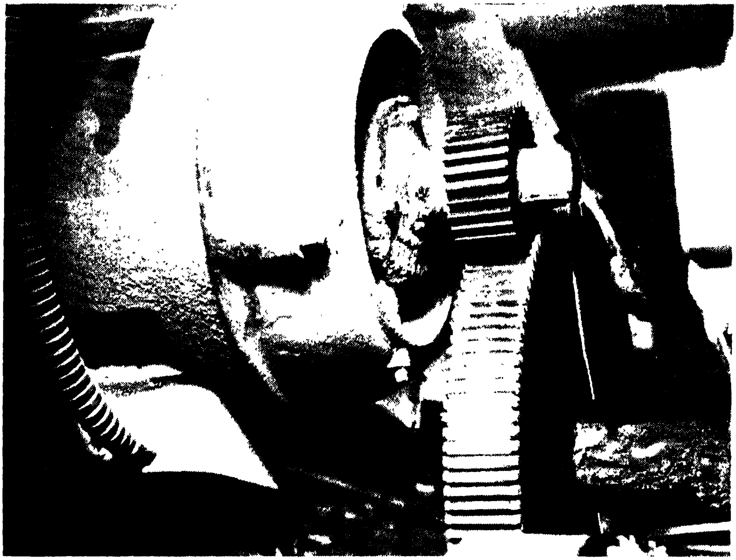


Fig. 96. Use of laminated gears in rolling mill[11]

A very interesting development in this respect has been made by Pasold and Kamphuys.[8] They suggested the use of knitted fabrics for the production of shaped laminated articles. In general, woven fabrics are not suitable for the formation of objects with double curvature. Knitted fabric will follow the curvature of the product and does not need to be cut or nicked for this purpose.

According to Brown, shapes of a much more complicated kind than the plain cylinders or flat sheets produced by rolling or pressing can be made by moulding. A steel tool containing cavities of the required shape is made in accordance with normal moulding technique and the impregnated material charged into the tool in suitably shaped sheets. The general technique is so to position the laminations that they confer strength to the article in the place where it is needed.

Laminated mouldings may be made from piles of paper, paper pulp, or of fabric. Generally speaking, only the simpler shapes can be produced from paper; this is because paper cannot be stretched to follow irregular contours. If undue moulding stress is placed on the material, fracture of the paper will result and the reinforcing effect of the laminations lost. A good deal more can be done with fabric; special cloths can be designed which will stretch and enable irregular shapes to be moulded.

Considerable ingenuity is exercised in designing the tool and in tailoring the charge, and each different article which is required to be moulded is the subject of careful study. Experience shows that meticulous attention must be paid to the direction in which the laminae are caused to run—the more complicated the shape the more difficult this becomes. Carefully designed mouldings of simple shape will possess the same mechanical properties as a flat sheet made from the same raw materials. Complicated shapes in which the laminations are contorted will have less mechanical strength.

It will be appreciated that this method of moulding results in a product stronger than can be produced by any other method of plastic moulding.

TABLE 61

PROPERTIES OF SHEET CONTAINING UNIAXIAL FLAX FIBRES COMPARED WITH STEEL AND ALUMINIUM ALLOY

Resin content, approximately 25%

	"Gordon Aerolite"	Stainless Steel	Aluminium Alloy
Density, gm. per cu. cm.	1·47	7·85	2·8
Tensile strength parallel to laminations:			
Tons per sq. in.	30	80	30
Kilometres	32	16	17
Compressive strength, tons per sq. in.			
Parallel to fibres	13	—	—
At 90° to fibres	6·2	—	—
Shear strength parallel to fibres:			
Tons per sq. in.	2·45	50	18
Young's modulus:			
Lb. per sq. in.	7×10^6	30×10^6	10×10^6

Properties of Laminated Materials. Laminated materials have all the best properties of both the resin and the continuous base. They are resistant to all forms of corrosion, being unaffected by solvents, oil, petrol, grease, organic acids, dilute mineral acids, alkalis, etc. They are unaffected by moisture under any conditions, and they withstand high temperatures without alterations in dimensions.

TABLE 62

PHYSICAL PROPERTIES OF PAPER LAMINATES, FABRIC LAMINATES, WOODS AND METALS

Material	S Specific Gravity	T Tensile Strength p.s.i.	S/T Ratio of Tensile Strength to sp. gr., p.s.i.	C Compressive Strength p.s.i.	C/T Ratio of Compressive Strength to sp. gr., p.s.i.	Modulus of Elasticity in Tension (E), p.s.i.	Ec Modulus of Elasticity in Compression, p.s.i.
Kraft paper . . .	1·35	16,000	11,800	38,000	28,100	$1{\cdot}7 \times 10^{6}$	$0{\cdot}83 \times 10^{6}$
Absorbent paper . .	1·35	11,000	8,150	31,000	23,000	$1{\cdot}05 \times 10^{6}$	$0{\cdot}6 \times 10^{6}$
Fine weave fabric . .	1·35	12,500	9,250	35,000	25,900	$1{\cdot}0 \times 10^{6}$	$0{\cdot}61 \times 10^{6}$
Coarse weave fabric . .	1·38	11,000	8,000	35,000	25,400	$1{\cdot}05 \times 10^{6}$	$0{\cdot}56 \times 10^{6}$
Stainless steel (18–8) .	7·85	185,000	23,600	150,000	19,100	30×10^{6}	30×10^{6}
Chrome molybdenum steel (heat-treated) . .	7·85	180,000	22,900	150,000	19,100	30×10^{6}	29×10^{6}
Aluminium alloy (24-St) .	2·80	62,000	22,100	40,000	14,300	$10{\cdot}4 \times 10^{6}$	$10{\cdot}4 \times 10^{6}$
Magnesium alloy (AM–585)	1·81	46,000	25,400	35,000	19,300	$6{\cdot}5 \times 10^{6}$	$6{\cdot}5 \times 10^{6}$
Aircraft spruce (Douglas fir)	·043	10,000	23,200	5,000	11,600	$1{\cdot}3 \times 10^{6}$	$1{\cdot}3 \times 10^{6}$
Birch plywood . . .	0·80	13,100	16,400	5,700	7,100	$1{\cdot}4 \times 10^{6}$	—
Cord material . . .	1·34	25,000	18,700	27,000	20,160	$2{\cdot}4 \times 10^{6}$	—
Gordon aerolite . .	1·43	45,000	31,500	24,000	16,800	6×10^{6}	—

TABLE 63

EXTRACT FROM BRITISH STANDARD SPECIFICATION NO. 436, 1940, SHOWING PERMISSIBLE STRESS FACTORS OF VARIOUS GEAR MATERIALS

Factor	Laminated Fabric	Cast Iron (high-grade, heat-treated)	Phosphor-bronze, Centrifugally Cast	0·15% Carbon Case-hardened Forged Steel	High Nickel-chromium Case-hardened Steel
Surface stress factor	560	2,000	1,000	9,000	12,600
Bending stress factor	4,500	10,400	10,000	20,000	50,000

Almost the outstanding feature is the extremely high ratio of strength to weight. The base material also confers a high degree of resilience on the laminate. Both compressive strength and flexural strength are impressive. They also withstand impact effectively. They have exceptionally good machining properties, a factor which makes them very popular for general engineering purposes. Good electrical characteristics such as extremely high dielectric strength also open up a wide field of applications.

Applications of Laminated Materials. As a result of this outstanding group of properties laminated materials have an ever-growing range of applications. They are particularly widely employed in the engineering industries. Perhaps the most spectacular use is for

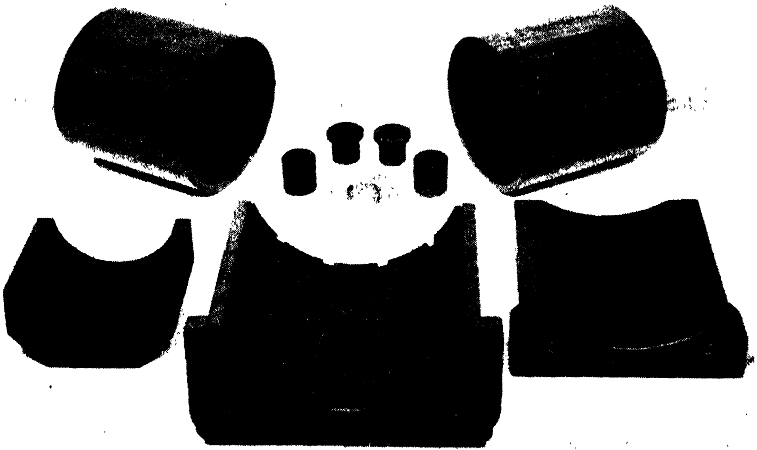


Fig. 97. Group of bearings machined from phenolic laminated materials[11]

heavy bearings. This application is a comparatively recent development, and is an admirable illustration of the exceptional mechanical characteristics. They are already employed as bearings on rolling mills of every description, for example, on steel rolling mills, brass rolling mills, paper mills, cement mills, and so on. Their use is very desirable because they save so much power, of the order of thirty per cent.

TABLE 64

REASON FOR THE USE OF LAMINATED BEARINGS[9]

(1) The material is light and can be easily handled
(2) Has the requisite strength
(3) Smooth bearing surface
(4) Good load-carrying capacity
(5) High resistance to impact
(6) Can be lubricated by any medium
(7) Non-scoring properties
(8) Low coefficient of friction
(9) Low thermal conductivity
(10) Low modulus of elasticity minimising high concentration of load
(11) Hard wearing

And on the economics side:
(12) Higher output
(13) Saving of power
(14) Lower lubrication costs
(15) Reduced maintenance costs
(16) Longer life, etc.

Its disadvantages include:
(17) Poor heat conductor
(18) Low temperature range of operation
(19) Experience of operators
(20) Initial cost of application
(21) No scrap value
(22) Not a universal application

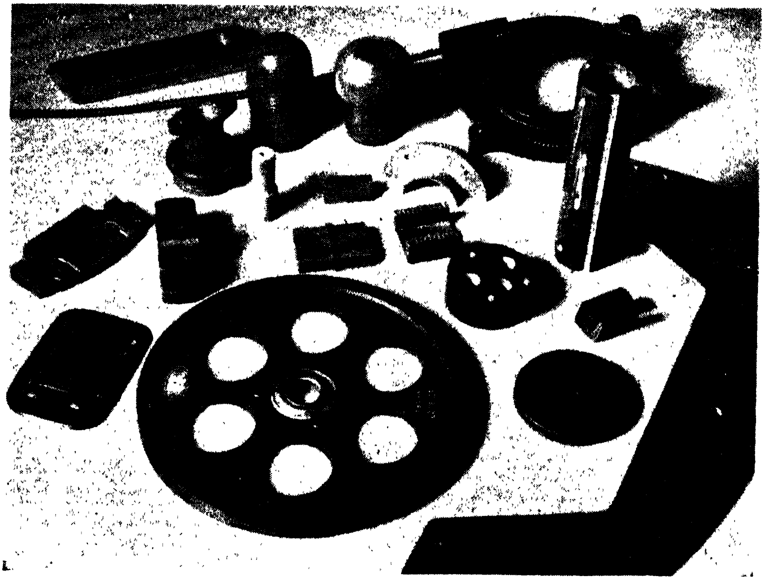


Fig. 98. Typical aircraft components from laminated material[11]

It has been stated that 80 per cent of German mills and 50 per cent of American mills are fitted with these bearings. For marine work they have replaced lignum vitae in many cases, for A brackets and for stern tubes. Such bearings are either made by machining out of slabs of laminated material or by building up of segments or strips.

Several additional features aid their use. For one thing they can be lubricated with water, and they can also be used in the presence of oil and chemicals without adverse effect. They are unusually resilient, being about forty times as resilient as steel. They will not adhere to metal, so that there is no chance of seizing, and there can be no risk of scoring those metal parts with which they come into contact.

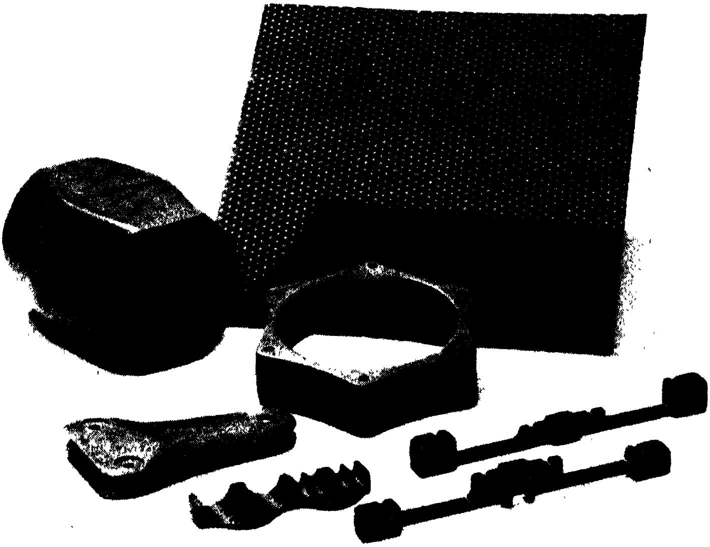


Fig. 99. Aircraft components machined from phenolic laminated materials[11]

Depending to a great extent on these characteristics is the growing use of laminated materials for gears. Gears of every description and design, spur gears, electrical gears, herring-bone gears, woven gears and so on, are made from laminated stock. Gears up to five feet in diameter have been produced. They are generally employed for silent gears, timing gears, electric clock gears, and also as gears for much heavier equipment. In addition they are also used for bushes, pinions, cams, wheels, etc.

In view of the excellent resistance to corrosion, another wide engineering field has been opened for them. For example, they are employed for gears, vanes, washers, discs, etc., in every form of petroleum machinery, chemical machinery, and textile machinery. In those instances where high temperatures are encountered the laminated materials are based on asbestos.

Laminated products in general have good electrical characteristics. They have high insulation resistance, low power factor, low moisture absorption, good dimensional stability, and so on, so that they are widely used in the electrical industry. Among the applications are panel boards, instrument bases, bushings, terminals, coil forms, and so on. Laminated components feature in high tension electrical equipment, in telephone apparatus, in radio equipment, and so on. Many millions of insulating components are based on laminated materials.

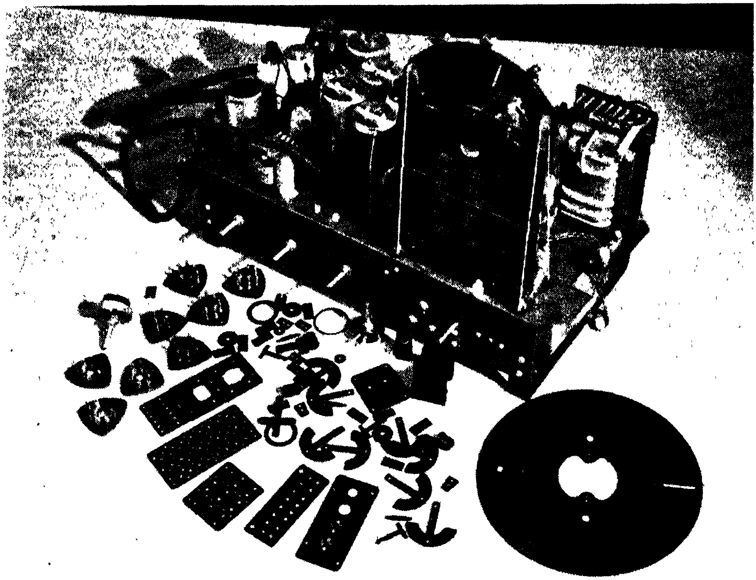


Fig. 100. Murphy radio chassis showing the components made from P.F. laminated and moulding materials[11]

Many of the products already mentioned, in one form of another are used in aircraft production. In this case while the physical characteristics are extremely important, there is the further consideration of the outstanding ability to withstand changes of humidity and temperature without alterations of dimensions. Typical applications include fairlead pulleys, aerial masts, instrument panels in addition to electrical uses.

The ability to have coloured or decorative surfaces of laminated materials have further increased the scope, notably for interior and exterior building purposes. They have found great application in public buildings, hotels and restaurants, for panelling doors and similar applications where the attractive decorative effects together with the permanent finish have proved extremely useful. By virtue of their resistance to heat and moisture they are also employed for table tops, counters, desks, and so on. There is also a growing tendency for their use as panelling in ships. It is interesting to note that examples of such materials are to be found in almost every telephone booth.

Laminated plastics have for some years been used for marine bearings. They have replaced lignum vitæ for stern tubes.

There are other methods for making impregnated paper sheets. In one process the synthetic resin may be applied to a paper base by adding the resin to the paper pulp whilst it is in the beating engine before the paper sheet is actually formed. By another method the constituents of the resin may be added to pulp and the resin condensed in the presence of the paper fibre, the resulting mixture being afterwards run on to the wire of the paper-making machine and formed into paper. The coated or impregnated filler forms the raw material for the subsequent processes.

Laminating at Low Pressure. The products so far discussed have been laminated under conditions of high pressure ranging up to one ton per sq. inch. However, recently the use of much lower pressures has become widespread. It seems evident that since a wrapped laminated tube is satisfactory for many purposes, then a similar technique could be utilised for larger and more complex products.

TABLE 65

GENERAL TYPES OF RESINS USED IN LOW-PRESSURE LAMINATING

	Resin Type	Hardening Temperature °C.	Moulding Time	Moulding Pressure lb./in.^{2}
Phenol-formaldehyde . .	Cold-hardening	20–60	30 min.–12 hr.	Contact–75
	Warm-hardening	60–105	15 min.–2 hr.	Contact–250
	Hot-hardening	140–180	5 min.–1 hr.	Contact–250
Urea-formaldehyde	Cold-hardening	20–60	10 min.–4 hr.	Contact–75
Thiourea formaldehyde	Warm-hardening	60–105	5 min.–15 min.	Contact–200
Melamine formaldehyde	Hot-hardening	125–150	5 min.–1 hr.	150–250

There are many applications where laminated products are admirably suited, but which do not need the extremely high strengths developed by ordinary laminating technique. As a result, many products are now made where an applied pressure of less than 100 lb. per sq. inch is employed during manufacture. In fact, in many cases even wrapping pressures of a few pounds per square inch are adequate. A further point of interest is that these methods have been adapted for use with resins and adhesives which set at much lower temperatures. Modified synthetic resins have been developed to give their best properties for the modified conditions.

Fig. 101. Cutting out impregnated paper for making wing tips[12]

Clearly the equipment required for such methods is much simpler. One great advantage is the ability to make curved and shaped articles which are impracticable by the ordinary method. Simple materials such as wood, plaster of Paris, and concrete lend themselves for mould construction in these circumstances. The only condition necessary is that the formers should be suitable for the application of the hydraulic pressure or any other form of pressure which is to be applied. Cold setting resins have been utilised to make such products which simplifies the process even further.

In essence the procedure is merely to wind or apply the fabric or paper on to the shaped former. The material used should be treated with resin prior to assembly. During this building-up process the resin should be as sticky as possible in order to hold the layers together Tape is widely used to assist in holding such structures together. It is evident that for many products successive strips of material will have to be applied. In any event when the assembly is together it may be coated with several layers of resins. When the article has been assembled parts which need no further external pressure may be directly baked.

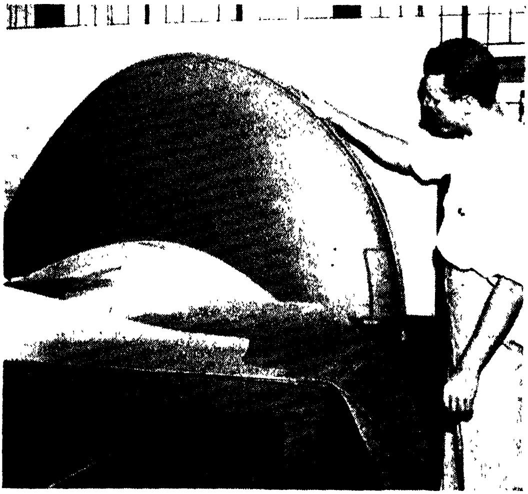


Fig. 102. The complete laminated wing tip

The sections which require the application of low pressures are then subjected to hydraulic pressure through some suitable medium such as a rubber bag or rubber sheet. One ingenious method for applying pressure and heat has been to use hot lead shot or sand, and there are other possibilities.[3]

Properties of Low Pressure Laminates. Laminated materials prepared with the use of low laminating pressures differ in a number of respects from normal laminates. The bonding agents, the resins, are not forced so well into the fibrous reinforcing agents. As a consequence these are able to take up much more water, nearer to the characteristic water absorption of the fabric or paper, etc. Tensile strength is not as high although it is still quite good, and the same applies to the flexural strength. The ability to withstand compression is similarly reduced, being lower than in the case of normal laminates. Since the material is less compact, as indicated by the much lower density, the strength and flexibility characteristics of the reinforcement tend to predominate

TABLE 66

EFFECT OF LAMINATING PRESSURE ON CANVAS CLOTH PHENOLIC[7]

Property	Laminated at 3 p.s.i.	Laminated at 30 p.s.i.	Laminated at 75 p.s.i.	Laminated at 2,000 p.s.i.
Tensile strength, p.s.i.	10,100	9,990	11,100	11,500
Flexural strength, p.s.i.	14,700	16,300	18,600	20,000
Compressive strength, p.s.i.	20,300	17,000	20,250	40,000
Izod impact, ft.-lb./in. of notch	2·3	1·85	4·17	4·7
Modulus of elasticity, p.s.i.	113,000	334,000	404,000	750,000
Specific gravity	1·13	1·16	1·20	1·35
24-hour H_2O absorption (untreated surfaces)	11·8	7·15	7·5	1·5

p.s.i.=pounds per square inch.

over those of the binder so that the products of low pressure lamination are rather tougher. It must be fairly evident that the laminations are not so tightly bonded together as in the case of high pressure laminates.

It is evident that these products will not have the strength of the high-compression articles, yet they possess characteristics which are adequate for numerous very important applications. The ease with which they can be made offsets other disadvantages. These products are not suggested for structural or semi-structural purposes, nor for any of the exacting uses such as gears, bearings, etc., which are of such outstanding importance in the field of laminated articles.

From the point of view of appearance they are not so attractive as high pressure laminates. The surface is less dense and lacks the high polish which characterises high pressure laminates. For many purposes these properties are of no significance.

Contact Resins. A new class of resins has begun to assume marked industrial importance. These are known by a variety of names including:

Contact pressure resins.
Cross-linking resins.
Polyesters.
Anhydrous thermosetting resins.
Allyl esters.

The importance of these resins is the introduction of entirely new methods of production. Articles such as laminated products and castings can be obtained at very low pressures eliminating the necessity for expensive and heavy equipment. "Contact pressure" is limited to the use of pressures of one atmosphere or less, as, for example, in the use of the well-known vacuum rubber bag technique, and all contact pressure resins should be capable of giving first-class laminates under these conditions. This does not mean that higher pressures should never be used, and in some cases pressures up to as much as 50 lb./sq. in. have been employed with advantage.

The materials are already used for contact pressure lamination; for low pressure lamination; for cast sheet, tubes, etc.; for impregnation; for surface coatings; for adhesives and for bonding.

The new materials depend upon double bond polymerisation which has been known for a long time. By the use of bi- or poly-functional monomers it is possible to set up a cross-linked network in the polymerising resin, leading to a thermoset rather than a thermoplastic type of compound. Recently these ideas have led to the introduction of a wide range of new compounds specially designed for laminating work.

Characteristics of Good Contact Resins. According to Williams[10] the properties required in a good contact resin for laminating are as follows:

(*a*) 100% *Solids content.* The resin should contain 100% solids, i.e. it should contain no solvent or diluent which does not itself interpolymerise with the resin. It must be water-white.

(*b*) *Low Vapour pressure.* The resin must have a low vapour pressure. This is particularly important as it is essential that little or no evaporation should take place during the laying up of the impregnated fabrics when the laminates are being assembled. Otherwise, serious losses of resin would take place, and toxic concentrations of vapour might be set up. It is also essential that the resin should not boil at the temperatures reached during the polymerisation cycle. Due to the heat of polymerisation these temperatures may rise to as much as 150° in some cases.

(*c*) *Absence of volatile products of reaction.* Under the conditions of polymerisation or curing, no volatile product should be formed as otherwise a bubbly laminate will result.

(*d*) *Viscosity.* The new resins are available in a suitable viscosity for impregnation purposes. Experience has shown that the most suitable viscosity for use with fabrics is usually in the region of 3 to 10 poises at room temperature. With paper a lower viscosity resin is to be preferred.

(*e*) *Stability and ease of catalysis.* The resin must be easy to catalyse, must have a long life in the uncatalysed state, and must have an appreciable pot life after the catalyst has been added. Resins are usually supplied in the uncatalysed state containing a very small quantity of stabiliser such as hydroquinone. Under these conditions, they are normally stable for at least six months, especially if stored in the dark and in comparatively cool conditions. Peroxide catalysts, usually benzoyl peroxide or lauryl peroxide are commonly used, in a proportion of about 1%, to initiate polymerisation and these must be dissolved in the resin prior to use.

Even at normal temperatures, some time after the catalyst has been added, thickening due to the start of polymerisation will take place, but, for obvious reasons, the pot life should be at least four hours and preferably considerably longer.

(*f*) *Speed of cure.* The resin should cure quickly under the conditions of polymerisation; i.e. the curing should not take longer than ½ hour at 100° for laminates up to ¼ inch thick. Some resins are more susceptible to poisoning than others. In particular, contact with rubber or exposure to the air during the curing cycle frequently tends to inhibit polymerisation. In many of the more recent resins this defect has been largely overcome, and the addition of cobalt accelerators of the type used with drying oil paints has been found to help considerably in minimising the effect of air poisoning.

(*g*) *Mechanical properties of the laminate.* In order that the laminate may have good mechanical properties, the liquid resin must cure to a hard rigid non-brittle solid. Resins which only give soft rubbery polymers are of little value and excessive cross-linking gives resins which are too brittle. The best mechnical properties are probably obtained when the elastic properties of the solid resin have values similar to those of the fibrous material being laminated. It is also important that the mechanical properties should be maintained over a wide temperature range and no undue softening should take place with temperatures over 100°. It is for this reason that cross-linking types are always to be preferred.

(*h*) *Miscellaneous properties.* There is a number of properties which are of greater or lesser importance depending upon the applications to which the laminates are to be applied. For example, the water absorption should be low and the dimensional stability under normal conditions of weathering should be good, and, in special cases, resistance to attack by chemicals may be important. In many uses, too, the electrical properties have to be considered.

Types of Contact Resins. There is a wide range of organic compounds from which resins can be prepared. The nature of the active double bonds and of the chain links between them can show wide variations, but the different types of resin which have been produced so far, all fall into one of the four following classes: (*a*) allyl, methallyl and crotonyl derivatives; (*b*) maleic acid derivatives or alkyd type resins; (*c*) acrylic derivatives; and (*d*) vinyl compounds.

(*a*) *The allyl class.* These compounds were some of the first which were introduced as contact pressure laminating resins. Probably the simplest is di-allyl phthalate. Another resin of this type is C.R. 39, which is the diallyl derivative of diethylene dicarbonate. Both these monomers are mobile liquids which require thickening if they are to be used as contact pressure laminating resins. While they are useful casting resins they are not particularly suitable for laminating work as the allyl group is not very active, and consequently the polymerisation time is unduly long; also they are very easily inhibited.

(*b*) *Maleic acid derivatives or alkyd type resins.* Many of the more popular and common resins fall in this group. It has long been known that esters of maleic acids, while difficult to polymerise on their own, will interpolymerise very readily with other double bond compounds. Further, maleic acid lends itself to the ready synthesis of comparatively short chain molecules with the maleic acid groups interspersed at intervals down the chain by condensation of maleic anhydride with various dihydroxy compounds; for example, maleic anhydride and ethylene glycol will condense together to give a chain in which the double bonds of the maleic acid groups are separated by a chain length of six atoms. Compounds of this type are very easily synthesised by the well-known technique used in making alkyd resins for paints, but in order to make them readily polymerisable they need to be mixed with some other monomer which is itself fairly readily polymerisable. The most common material used is styrene which can be mixed with the alkyd resin in proportions of up to about 50%. Such mixtures will polymerise rapidly at temperatures of the order of 100° and in this respect are considerably superior to the allyl type. The chief drawback of this class is the volatility and toxicity of the styrene.

(*c*) *Acrylic type resins.* Instead of relying on the copolymerisation of the maleic double bond in polyester chains with monomers, such as styrene, cross-linking can also be brought about by the polymerisation of chain molecules having acrylic groups attached at suitable points. The possible varieties in such chain molecules are, of course, very great, but the type of structure which can be produced can be illustrated by two simple examples.

In the first, hydroxy-ethyl-methacrylate is reacted with any molecule having terminal carboxy groups to give a dimethacrylate. A simple case would be the reaction with adipic acid to give dimethacrylyl-glycol-adipate.

In the second, a basic chain with terminal hydroxy groups is taken, such as diethylene-glycol, which can be reacted with acrylic acid to give diethylene glycol di-acrylate.

Resins in the acrylic class are fast curing and inhibition by air or rubber is considerably less than with the types previously mentioned. In addition to being cured alone, they can also be interpolymerised with other monomers if desired, to give products with varied properties.

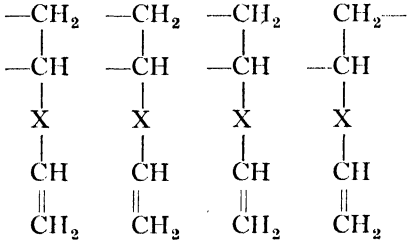
(*d*) *Vinyl compounds*. On similar lines to the foregoing the synthesis of chain molecules with terminal vinyl groups gives rise to another class of contact resins. Staudinger illustrated the cross-linking effect obtained on polymerising mixtures of di-vinyl benzene and styrene. The di-vinyl derivatives of di-basic acids (e.g. di-vinyl sebacate) constitute further examples of this series.

In practice, however, few, if any, contact resins have actually been produced based on this type of structure. Styrene itself is the vinyl derivative which has been most widely used, but only as an interpolymer constituent. It must again be emphasised that it suffers the disadvantage of being rather more volatile than is desirable. More recently the chloro-styrenes have been introduced and although they are expensive they do have the advantage of a considerable lower volatility.

Estevez[5] has described how, in general, all these resins can be represented by two types:

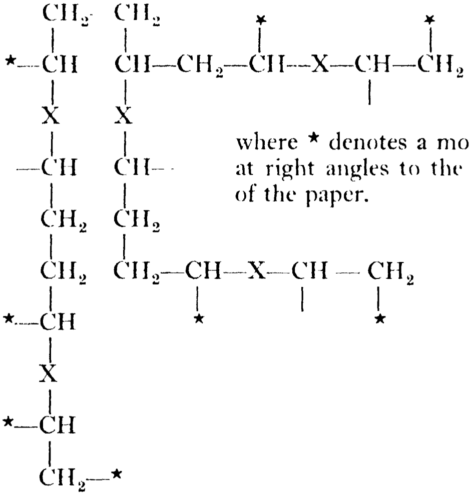
(1) The normal cross-linking resins which can be illustrated by the generalised formula: $CH_2{=}CH{-}X{-}CH{=}CH_2$.

Hence



$$\begin{array}{cccc}
-CH_2 & -CH_2 & -CH_2 & CH_2- \\
| & | & | & | \\
-CH & -CH & -CH & -CH \\
| & | & | & | \\
X & X & X & X \\
| & | & | & | \\
CH & CH & CH & CH \\
\| & \| & \| & \| \\
CH_2 & CH_2 & CH_2 & CH_2
\end{array}$$

leading to



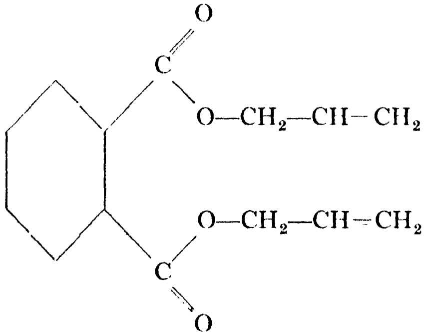
where * denotes a molecule at right angles to the plane of the paper.

Thus, because of the two double bonds per molecule, a three-dimensional network results, giving a substantially insoluble and infusible thermosetting resin.

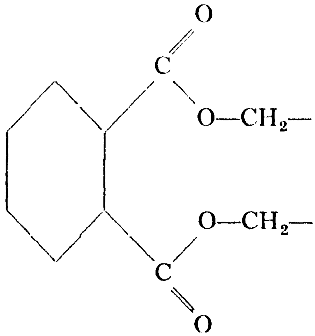
(2) The so-called "vulcanised cross-linking" resins. In these the liquid form consists of two chemical species, one of which is a monomer of a potentially reactive resin, and the other a long chain molecule containing double bonds, but generally incapable of polymerisation of itself with or without a catalyst.

Under the influence of heat and a catalyst, the double bonds of the long chains open out, and the chains are cross-linked one to another by the second chemical entity, which again results in a thermosetting solid product. Typical examples of these two classes are:

(1) Diallyl phthalate (A) below



A



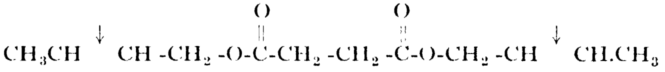
B

Here the grouping (B) takes the place of the X in the above generalised formula, and the cross-linking occurs exactly as shown there.

(2) The system recently mentioned in B.P.544,057, consisting of diethylene glycol maleate and dicrotyl succinate,

$$OH\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}C\text{-}\overset{\overset{O}{\|}}{C}\text{-}C\ \overset{\downarrow}{\ }\ \overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2OH$$

and



$$CH_3CH\ \overset{\downarrow}{\ }\ CH\text{-}CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH\ \overset{\downarrow}{\ }\ CH.CH_3$$

in which, on heating in the presence of a catalyst, the double bonds shown " ↓ " open up; and the chains of the di-glycol ester are linked in the middle by the ends of the crotyl ester molecules, so forming a cross-linked network.

Applications and Laminating Techniques. In considering uses of the new contact resins it must be remembered that at the present time, and probably for some considerable time in the future, they will be more expensive than the conventional phenolic and urea resins, and consequently they can only be employed economically in specialised uses where their advantages outweigh their extra cost. These advantages are:

(1) *Great ease of application and the absence of any need for expensive equipment.* The fact that the resins can be used at contact pressures means that no expensive presses are required. The resins are also extremely easy to handle. The fact, too, that the resins after impregnation are immediately ready for use and do not require any drying treatment is a great convenience. The rapidity of cure at low temperatures of the order of 100° means that quick cycles can be obtained and is another important factor in the economics of the process.

(2) *Colour.* The best of the contact resins are water white and consequently light colours and attractive printed designs can readily be manufactured. In this respect the resins are far superior to the phenolic types and a first-class surface finish can be prepared at lower pressures than with the urea and melamine resins.

(3) *Use in sandwich construction.* The importance of this type of structure has been fully recognised recently and the contact resins offer many advantages when used for laminating strong skins on either side of a low density core. Most of the common types of core will not stand up to the full pressures needed for laminating the conventional resins and the sandwich structures can only be built up by glueing together the finished core and skin

components, whereas with the contact resins the complete sandwich construction can be made in one process.

The advantages outlined above have enabled the following types of application to be successfully developed:

(*a*) The construction of large shaped articles, such as boats, articles of furniture, suitcases, etc., where due to the size and double curvature the use of conventional laminating presses is quite out of the question.
(*b*) The production of continuous laminated sheet, which is a comparatively simple process once the need for pressure is eliminated.
(*c*) The surface finishing of panels, etc., where the good colour and quick cure enable attractive and cheap effects to be produced.
(*d*) The construction of strong light-weight structures usually of the sandwich type, as, for example, radomes for aircraft.

Types of Fabric which may be used. Satisfactory laminates can be prepared with almost any type of fabric. Much effort has been concerned with glass laminates as these enable articles of very high strength to be manufactured. Cotton cloth is quite suitable. Asbestos fabrics have also been used successfully. Paper, on the other hand, is not normally very suitable, probably because many of the resins are rather too viscous for thorough impregnation of the close fibre structure. Apart from the use of cloths, felts or mats can also be used and the use of glass fibre mats is a particularly interesting development. It is possible that these mats will eventually be produced much more cheaply than woven glass cloth, but that when properly laminated they will give structures fully equivalent in strength to those obtained with the cloth.

Manufacturing Techniques. The first step in the use of the resins is to catalyse them. Full instructions are given by all the various manufacturers and this step usually merely consists of dissolving the benzoyl peroxide or other catalyst in the resin, in some suitable stirred pot.

Impregnation of fabric is usually carried out by running it through a bath of the resin followed by suitable squeegee rollers adjusted to give the required resin content to the cloth. For continuous laminated sheet the impregnating bath is usually integral with the rest of the laminating equipment, but for other work it is usual to reel up the impregnated fabric and store it in the wet rolled condition until it is wanted. When making shaped articles tailored fabric will be required and this can be cut from the wet impregnated cloth. Alternatively, the cloth can be tailored in the dry condition, but this makes impregnation more difficult, although the process can be carried out by dipping the tailored pieces or by brushing the resin on to them.

TABLE 67

PROPERTIES OF TYPICAL CONTACT RESIN

	Type of Laminate	
	Glass Fibre	Cambric
Ultimate tensile strength in p.s.i.	32,500	6,250
Young's Modulus in bend p.s.i.	$2 \cdot 0 \times 10^6$	$8 \cdot 0 \times 10^5$
Bend strength in p.s.i.	40,000	15,000
Compression strength in p.s.i.		
Parallel	17,000	25,000
Perpendicular	52,500	30,000
Density	1·72	1·33
Volume resistivity ohm/cm.	$3 \cdot 3 \times 10^{13}$	$9 \cdot 1 \times 10^{11}$
Water absorption per cent.—Specimens $2 \times 2 \times \frac{1}{4}$ in.		
After 1 day 20 deg. C.	0·42	0·58
After 1 week	1·3	2·6

After the impregnation stage the technique naturally varies according to the type of product being manufactured. For the production of continuous laminated sheet, probably the simplest method is to pass the requisite number of plies through a pair of rollers which squeezes them together and at the same time applies a surface layer of cellophane on either side. The cellophane overlaps the cloth at either edge where it is gripped by some form of stenter arrangement. The whole assembly then runs continuously through an oven where the temperature is brought up to 100° or higher. At the far end of the oven the cellophane is stripped off and the edges of the board are trimmed. The sheet can then be cut as desired.

Casting with Contact Resins. Hard tough mouldings of clear or coloured sheets, rods, tubes and shaped articles may be cast and polymerised at room temperatures. They give products with good surface hardness and free from crazing.

With one proprietory material a polyester casting is carried out in the following manner. There are six ingredients:

1. Resin.
2. Modifier (usually styrene monomer).
3. Catalyst.
4. Accelerator.

and two optional ingredients

5. Filler (to strengthen or to cheapen the product).
6. Dyestuff or pigment.

The catalyst is invariably a peroxide, generally benzoyl peroxide. This initiates cross-linking and promote the polymerisation. The accelerator is a solution of a cobalt compound such as cobalt naphthenate.

	White Casting parts by weight	Clear Casting parts by weight
Resin . . .	100	100
Modifier . . .	40	10
Catalyst . . .	1·5	0·5
Accelerator . .	2	1·5
Chalk . . .	75	—
Alumina . . .	12	—

These compositions gelled in 20 minutes at 25° C. Actually the setting divides into three stages, i.e. gelling, curing and final hardening. The higher the temperature the faster the cure.

Contact resin castings are resistant to fats, oils and greases and most chemicals. They are affected by acetone. They have a very low moisture absorption and the electrical properties are quite good. They are non-tracking. For this reason they find use in coil impregnation where the solvent-free character is invaluable.

REFERENCES

1 Bakelite, Ltd. Technical Literature.
2 De Bruyne. Technical Literature of Aero Research, Ltd.
3 British Thomson-Houston Ltd., B.P. 401,276.
4 Brown, Trans. P.I., 1947, April, p. 22.
5 Estevez. Trans. P.I., 1948, p. 79.
6 Goldman and Olsen. *Mod. Plastics*, 1943, May, p. 100.
7 Nelson and D'Alelio. *Gen. Electric Rev.*, 1943, **46**, 483.
8 Pasold and Kamphuys. B.P. 555,669/1943.
9 Phillipe. *Plastics*, 1940, **4**, 3.
10 Williams. *Chemistry and Industry*, 1947, p. 367.
11 Photographs by courtesy of Bakelite, Ltd.
12 ,, ,, *British Plastics*.

CHAPTER XII

PLASTICS IN LAMINATED WOOD

PERHAPS the most important field in which synthetic resins feature as bonding and reinforcing agents is in conjunction with wood in its various forms. The excellence of wood flour as filler has already been considered. Wood in a continuous form promises to become even more important. In particular, synthetic resins have revolutionised the plywood industry. Plywood prepared with synthetic resins have opened up completely new territories for the further and more convenient utilisation of wood.

The ability to use heated presses in such manufacture offers very considerable production advantages. Since multiple platen presses can be used with many apertures, and a number of stacks of veneers may be assembled in each aperture, a large output can easily be attained. Thus a press may have twenty platens ranging up to eight feet by twelve feet in platen size. Clearly many thousands of square feet of plywood per day can be handled by such a unit. The process is extremely rapid since there is no necessity for a long period of standing for the glues to set. The use of synthetic resins reduces the time required for gluing from a matter of days to minutes. This factor offsets any marked difference in the cost of the various adhesives. On the other hand this process requires reasonably skilful operatives since there are a number of variable factors which must be carefully watched. The important factors are the moisture content of the veneer, the temperature, pressure, and time. The work of Perry in this field of activity has been outstanding.[8]

The possibilities of plywood for structural purposes and building purposes generally have been enormously enhanced by this development. By virtue of the strength associated with light weight, plywood is enabled to stand comparison with many of the older constructional materials. The possibilities are further enhanced by the ease with which panels can be assembled by means of scarf joints to give continuous lengths, in which the join is not a source of weakness.

Wood is one of the most widely used materials of construction. This is due to its ready availability, the ease with which it can be worked, its general mechanical and physical characteristics, and its inherent beauty. However, it has very marked shortcomings. By its very nature wood has strength only in the direction of the grain. It tends to split and has irregularities. It is subject to dimensional changes under different climatic conditions. Being greatly affected by water, it swells or shrinks according to the amount present. It is also inflammable.

From prehistoric times efforts have been made to overcome these disadvantages. These efforts have taken many familiar forms, for example, the application of paints or varnishes, impregnation of wood, and so on. The outstanding method of overcoming the grain effect is, of course, by the assembly of thin strips of wood or veneers into the form of plywood. This art was discovered by the Egyptians, who cut wood into layers, assembled them in opposite directions, whereby the strength was distributed equally. They employed casein and animal glues for their adhesives. The success of their efforts is evident from the excellent preservation of many of their examples, although it must be evident that they have been preserved under the best conditions.

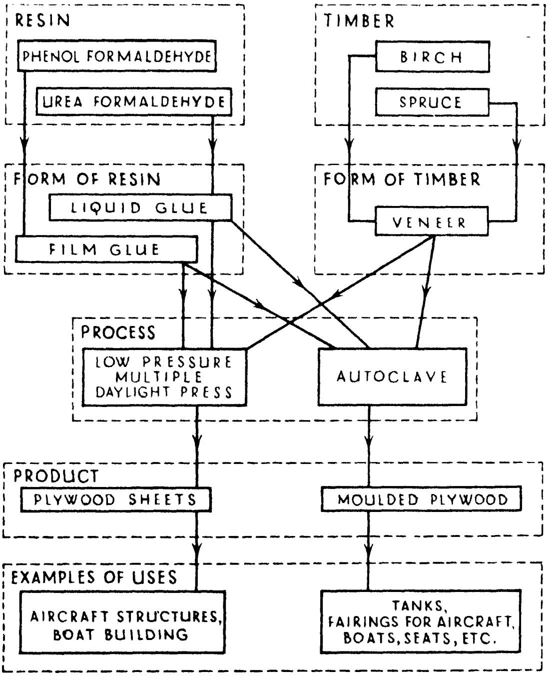


Fig. 103. Preparation of resin-bonded plywood[5]

Plywood, as commonly known to-day, is of recent origin, about seventy years old. Compared with solid wood, it is slightly heavier and harder. Its physical properties are rather better and far more uniform. It is much less affected by water.

It still has many disadvantages. The joins or glue lines are sources of weakness, and under adverse conditions lead to ready delamination. The outstanding difficulty has been the poor water resistance of most adhesives. The types used include animal or fish glue, casein and vegetable glue, such as starches. All these are widely employed at the present time. The best type is animal blood, which can be coagulated by heat, and is then found to give a good water-resisting bond. On the other hand, this is attacked by moulds and fungi, and is variable. Almost the chief disadvantage is that these adhesives are slow in processing and involve prolonged conditioning.

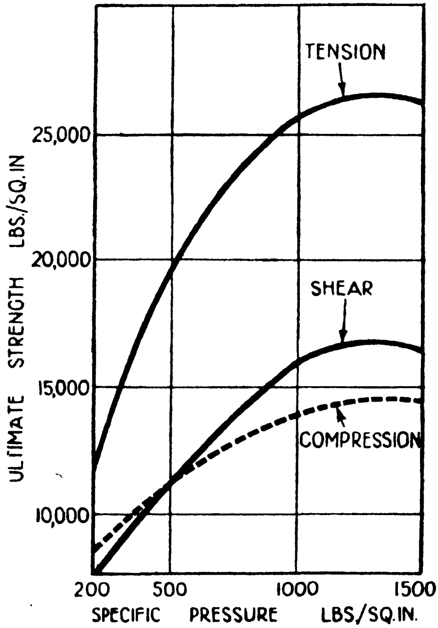


Fig. 104. Behaviour of laminated plywood[5]

This difficult problem has been completely solved by the use of synthetic resins. Phenolic resins based on phenol and cresol are employed, sharing the field with urea-formaldehyde resins. Lately, melamine resins have been proposed for this application. Thermoplastic materials also have a limited use, polyvinyl formal in particular having attained prominence.

Applications of Resin-bonded Plywood. Resin-bonded plywood has assumed great importance commercially for numerous purposes. In the first place it is very popular as panels for ships, railway coaches, and general construction purposes.

TABLE 68

CHARACTERISTICS OF A FEW METALS, WOODS, AND LAMINATED WOOD

	Specific Gravity	Weight per cub. ft. lb.	Ultimate Tensile Strength lb./sq. in.	Ultimate Com-pressive Strength lb. sq. in.	Ultimate Shear Strength Rt. L. fibre lb./sq. in.	Ultimate Shear Strength Parallel Fibre lb./sq. in	Modulus of Elasticity lb. sq. in.	Linear Coefficient Thermal Expansion per deg. F.	Tensile Strength divided by Weight
Cast Aluminium .	2·56	159	15,000	12,000	12,000	12,000	11×10^6	12×10^{-6}	94
Cast Iron . .	7·20	449	15,000	80,000	18,000	18,000	12×10^6	5×10^{-6}	33
Cast Brass . .	8·40	536	24,000	30,000	36,000	36,000	9×10^6	9×10^{-6}	44
Cast Gun-metal .	8·85	553	32,000	20,000	—	—	10×10^6	10×10^{-6}	57
Cast Copper .	8·82	550	24,000	40,000	30,000	30,000	10×10^6	9×10^{-6}	43
Laminated Wood .	1·4	87	34,000	23,000	7,000	3,000	$3·7 \times 10^6$	12×10^{-6}	390
Wrought Iron .	7·85	480	48,000	46,000	40,000	40,000	27×10^6	6×10^{-6}	100
Dural . . .	2·8	175	56,000	56,000	35,000	35,000	10×10^6	11×10^{-6}	320
Structural Steel .	7·8	486	60,000	60,000	50,000	50,000	29×10^6	6×10^{-6}	123
Spruce . .	0·48	30	9,000	4,500	1,200	800	$1·4 \times 10^6$	—	300
Beech . .	0·75	47	18,000	9,000	2,140	1,250	$1·9 \times 10^5$	—	383
Ash . . .	0·77	48	15,000	7,000	1,200	800	$1·7 \times 10^6$	—	312
Oak . . .	0·8	50	13,250	5,760	3,890	1,080	$1·5 \times 10^6$	—	265

The outlets for these materials in future building activity are quite obvious. The importance of blockboards for the making of doors and substantial wall-panels will probably expand considerably. The surface finishes of plywoods include all types and textures that can be desired by the architect, and no doubt even greater varieties of fabric-surfaced plywoods will be produced.

There is tremendous interest in the possibilities of utilising such sheets for the prefabrication of houses. Numerous small huts and other structures have been prefabricated on the basis of resin-bonded plywood. The material has the necessary characteristics which render it very suitable for such applications.

These forms of plywood have also found wide use in the manufacture of furniture. Delamination of veneers has always been a disadvantage in using plywood for furniture. Resin-bonding has obviated this disadvantage, and has also facilitated manufacture. Urea-formaldehyde resins are extremely popular in every form for furniture production, and are used by hot pressing and in the cold throughout the industry. The utilisation of such wood for aircraft and marine purposes is a major industry of outstanding importance.

Moreover, it is possible to preform plywood during the bonding operation. As a consequence a large number of new and interesting products have been developed having curvature. So far much of this work has centred on aircraft and marine production. There are limitations to the shapes which may be attained. These of course will depend on the strength of the veneer, the direction of grain, and similar characteristics. While it has been known for some time to make very simple shapes the technique for making more complex curved sheets has only comparatively recently been developed.

TABLE 69

STRENGTH COMPARISONS BETWEEN WOOD VENEER AND PLASTIC MATERIALS[11]

Material	Sp. Gr.	Ultimate Tensile tons/sq. in.	Ultimate Compressive tons/sq. in.	Youngs Mod. lb./sq. in. $\times 10^6$
General purpose phenolic wood flour filled	1·3	3·00	4·50	0·80
Fabric base phenolic laminate	1·34	8·00	8·00	1·20
Spruce veneer plywood	1·4	23·00	16·00	4·00

Resin-bonded Tissue Paper Interlayer. The outstanding contribution was the application of tissue paper impregnated with suitable resins as the bonding medium. This has been attributed to Weber ar Hengstebeck, who prepared the material in 1920. The paper, 1/1000 inc thick, is passed into a solution of phenolic resin. The solvent is drie off and recovered, leaving a dry, fully-impregnated tissue paper abo 2/1000 inch thick. This is employed as the adhesive material. The fil ordinarily contains two parts resin to one part paper. The sheets a extremely stable. Veneers of wood are assembled into stacks, bein interleaved with suitably-cut sheets of impregnated tissue. No moistu or solvent is involved. The assembly is then subjected to heat an pressure in multi-daylight presses. The result is a plywood pane which is an almost indestructible material.

It is resistant to moisture, has great strength, withstands corrosion o every description, is unaffected by insects, moulds, or bacteria. Th outstanding feature is perhaps that the glue line is the strongest part o the assembly. Advantages for the use of impregnated tissue paper are

(*a*) The uniform spread of resins
(*b*) Dry processing
(*c*) Great simplicity and cleanliness
(*d*) Light-coloured veneers may be used without fear of staining.

The best known type in this country is Tego[9] gluefilm, which has had a most profound influence on the plywood industry. Tego gluefilm is used under the following conditions:

(1) Platen temperatures are between 140° and 150°C., the higher figure being the more satisfactory.
(2) Pressure range generally between 120 and 300 lb./sq. in.
(3) The time which the stack must remain in the press varies from 6½ minutes for a thickness of 1 mm. rising by about 1 minute per millimetre, e.g. for 15 mm. the time is 20 minutes.
(4) The moisture content of the veneers should be controlled within 8 to 12 per cent, if the maximum joint strength is to be obtained.

TABLE 70

PRESSURE FOR USE WITH "TEGO" GLUEFILM[9]

Wood	Pressure lb./sq. in.
Pine, fir spruce	120/140
Alder, poplar, basswood	140/150
Oak and high density woods	150/200
Thin stock of hardwoods such as birch, maple, beech, oak, etc.	200/300

This procedure achieved fairly rapid popularity, although it was always limited by the number of suitable presses available. In recent years there has been a considerable increase in the number of presses in order to meet expanding demands.

Use of Adhesive Solutions. While this sheet form of synthetic resin adhesive gives an extremely elegant process there are other methods of achieving a similar result. There are many other adhesives. Solutions are employed along the same lines as the conventional adhesives, while the synthetic resins are also available in powder form. In essence, any suitable resin may be dissolved in alcohol or water, applied to the veneers, the solvent dried off, the veneers laid up and bonded under heat and pressure in the same way as with the tissue. The products obtained in such a manner are comparable to those obtained with the impregnated film. As in the case of phenol-impregnated papers, the typical press treatment involves heating for ten minutes at 170° C. or half an hour at 140° C. under a hydraulic pressure of from 125 to 250 lb. per sq. inch. The pressure used depends on the wood; higher pressures are used for hard woods, lower pressures for soft woods, e.g. 125 lb. per sq. inch on spruce, but 250 lb. per sq. inch on birch.

At the end of the heating period the panel is cooled in the press, and is only then removed. Removal while hot will inevitably cause buckling. At 170° C. $\frac{1}{16}$ in. plywood requires only five minutes, whereas $\frac{5}{16}$ in. needs twelve minutes. The adhesive bond is completely waterproof and will withstand boiling or prolonged exposure without any tendency for delamination.

Powdered phenolic adhesives have recently arrived which can be readily dissolved in water, to give stable solutions, which can be used at 110° C. to give really satisfactory waterproof bonds.

Introduction of Urea-Formaldehyde Resins as Adhesives. The fact that temperatures and pressures involved in using phenol-formaldehyde adhesives were rather high and not readily available to many woodworking concerns was a drawback to rapid expansion, so that the appearance of suitable urea-formaldehyde resins in 1937 was welcomed. The bonds obtained are not in general quite as good as with phenolic resins. They will not stand up to boiling water for very long periods yet they are still far superior to the standard adhesives.

They have an advantage over phenolic resins in that they can be extended with fillers such as flour, which gives a much cheaper product.

In recent years there has been a demand for cheaper resin adhesives which could be used for less exacting purposes, for example, the production of furniture, radio cabinets, and so on. In such cases the high sheer values and extreme resistance to water were relatively unimportant.

They may be cured in a shorter time, and at much lower temperatures than those worked with phenolic resins, for example, temperatures of 120°C. are quite adequate using hydraulic pressures of 200 lb. per sq. inch. Even lower temperatures and pressures can be used, down to 90° C. and 40 lb. per sq. inch although the heating cycle will then be correspondingly longer.

The principal technical advantages of urea-resin adhesives in the manufacture of plywood are:

1. Low pressure and low temperature pressing conditions enable many ordinary veneering presses to be used in the production of high-quality plywood.
2. Ordinary air-dried veneers are being used with complete success, irrespective of slight differences of 1 or 2 per cent moisture content. Urea-resin adhesives are initially water soluble, therefore strict control of moisture is not necessary.
3. Owing to the lower temperatures and pressures employed urea resin-bonded plywood suffers little "burnishing" or "case-hardening" of the surface veneers. Consequently it is easy to glue in subsequent operations and does not require sanding to open up the surface. This is of considerable importance in aircraft construction.

Low Temperature Manufacture of Plywood. The introduction of urea-formaldehyde resins for bonding plywood immediately introduced the possibilities of low temperature pressing, for the setting of the resin could be accelerated by means of acid catalysts so as to function at almost any desired temperature. Already a number of urea-formaldehyde adhesives are available which may be set in this manner. So that plywood may be pressed at temperatures above 90° C., at temperatures below 90° C, and at ordinary ambient temperatures. The bond obtained by such methods are as water-resistant and as durable as when prepared by high temperature methods. The ability to make such products at ordinary temperatures open up completely new possibilities which previously were not practicable. Following this trend phenolic resins have also been developed which can be set by catalysts, and which acquire the ultimate hardness after a few hours' standing.

During the last year or two the utility of plywood assemblies has been even further extended by the use of low hydraulic pressures as well as low temperatures.

Low pressure lamination is now a very popular technique. It is fairly clear that the bonds obtained by low pressures are not as strong as when high pressure is employed. Nevertheless they are adequate for many applications. Adhesion in the cold along these lines does not offer such possibilities for mass production since there is a considerable time factor involved. The production economies of hot pressing do not apply. On the other hand it is a serviceable procedure which can be utilised in the absence of expensive, highly specialised equipment such as presses. It does open up possibilities for making articles with contours.

Newer Heating Methods. The preparation of thick plywood assemblies introduces complications in hot pressing owing to the poor conductivity so that curing takes a long time and is uneven throughout the assembly. As a result outside veneers are excessively heated, while the interior is undercured.

Other things being equal it can be stated that the lower the external temperature used the better the product. Two alternative procedures have been evolved which appear to be very satisfactory.

The use of high frequency electrostatic fields is spreading rapidly. This takes advantage of converting high frequency electrical energy into heat by means of the dielectric loss of the material. The assembly is placed between electrodes, and a suitable temperature is developed in a very short time, even with assemblies several inches thick. The resin becomes hotter than the wood, which is an advantage because the latter does not then lose moisture. Such a method is clearly very flexible and lends itself to uses other than in the sheet form.

This equipment is now applied to thick plywood bonded with thermosetting resins, such as the urea and phenol-formaldehyde types. Recently one of the largest units of high frequency equipment was installed in a United States plywood plant, having a capacity of 600 k.v.a. input. Now this plant is turning out stacks of phenol resin-bonded plywood panels that are twelve inches thick and four by ten feet in area at the rate of 15 bundles per hour. A further advantage of this process is that while the stack is uniformly heated, panels of different thicknesses may be produced by eliminating bonding between the faces of the panels.

Electrically Conducting Glue. Gallay[3] incorporated carbon black into phenolic resin adhesives and thereby made the glue a conductor. Another alternative was to interpose a loose woven fabric upon which the conducting filler was deposited. In either case the glue becomes hot when an ordinary low voltage current is passed through it. It rapidly becomes hot enough to set to the final infusible condition giving a bond of full strength. The wood veneers are pressed together by any convenient method, e.g. presses, clamps, etc. The feature of this procedure is that heat is only applied to the adhesive layer itself, none being wasted on the wood. The condition of the wood, particularly the troublesome moisture content, is of no consequence with this procedure.

Wire Mesh Heating. The other procedure which has acquired some practical significance is the use of fine wire mesh acting as part of the adhesive layer; an electric current is passed through, and adequate heat is developed to cure the resin. In both these instances hydraulic pressure is applied to the assembly. One method is the Tegowiro method for bonding rough massive wood.

In the hot wire method, a conducting wire mesh is embedded in the synthetic resin. An electric current is passed through the mesh whereby a high temperature is developed in the resin layer sufficient to cure it in a few minutes. One type of mesh was a spot welded wire 6 mms. by 40 mms. mesh, the wire being 12 mils diameter. Another type was a zigzag woven assembly of the same wire, the wires being separated by adhesive paper. The required sections are cut out of these wires and the current passed through. Various types of wood have been cured by this method, giving satisfactory results. It is effective even with thick sections of wood which may be fairly rough and what is more important, which may contain a very high proportion of moisture, up to 30 per cent.

According to one investigation by Egner,[2] the clamping pressure for soft wood was of the order of 100 lb. per sq. inch, and for hard wood of the order of 200 lb. per sq. inch. Current of 30 amps for each 10 longitudinal wires in the mesh was suitable. Voltage drop required was about 9·1 volts per metre of wire net. They attained temperatures of the order of 100°C. after 4 minutes passage of the current. This method is still in the early stages and can be expected to have a very profound influence on future development.

Improved Wood. There have been other significant improvements in wood by association with plastics. New types of materials known as *improved wood*, *super wood*, *compressed wood* or *compreg* have become available. In these instances the whole assembly of wood veneers is made denser by subjecting the wood to high pressure whereby it is compacted, and the wood layers are also impregnated with the resin. The result is that compared with ordinary plywood of the same thickness there is a greater number of layers of synthetic resin holding together densified compressed wood.

This has a profound effect on the strength and general characteristics of the material.

According to Livingston Smith,[5] by doubling the density of wood

TABLE 71

LAMINATED DENSIFIED WOOD COMPARED WITH A FEW NATURAL TIMBERS (ASH, OAK, BEECH, SPRUCE, ALSO WITH DURAL AND STEEL)

Material	Ash	Oak	Beech	Spruce
Specific gravity	·77	·8	·75	·48
Tensile strength	15,000	13,250	18,000	9,000
Compressive strength	7,000	5,800	9,000	4,500
Young's modulus	1·7	1·5	1·9	1·45
Shear strength*	1,200	3,900	2,140	1,200
Shear strength†	800	1,080	1,250	800

Material	Dural	Steel	Laminated Wood	
Specific gravity	2·8	7·75	·9	1·3
Tensile strength	56,000	78,000	23,000	32,000
Compressive strength	56,000	65,000	14,500	21,000
Young's modulus	10·1	30	2·8	3·7
Shear strength*	35,000	50,000	4,550	7,000
Shear strength†	—	—	3,100	4,100

Note: (1) All strengths are ultimate stresses in lb./sq. in. (2) Young's modulus given as $E \div 10^6$ lb./sq. in. (3)* Denotes shear strength perpendicular to fibres. (4) † Denotes shear strength parallel to fibres.

the mechanical characteristics are trebled. The cellular structure of the wood is rendered less effective for taking up moisture.

A few of the reasons for the popularity of this and other forms of laminated woods are:

(1) Lightness.
(2) High strength/weight ratio.
(3) It has good moisture, acid, and insect resisting characteristics.
(4) It can be manufactured in a few hours.
(5) It is easier to work than metals, and articles made from it can be modified at will.
(6) It can be handled by woodworkers.
(7) Improved compressive strength and hardness.
(8) Better electrical resistance.

The character of the adhesive plays a great part in determining the properties of the final product. For example, resin-impregnated tissue paper is often employed as bonding agent. In such instances the resin cannot impregnate the wood layer to any appreciable extent so that any densification is largely obtained by straightforward compression of the wood itself. The maximum amount of resin which can be present is about 12 per cent. The products obtained therefore have properties which are predominantly those of wood which has been reinforced with plastic. *The wood characteristics predominate.*

On the other hand where liquid adhesives have been employed the wood may take up large quantities of the resin and consequently when subjected to heat and pressure, greater densification occurs in which the wood and resin are more intimately and firmly joined. In these cases the product has properties which are predominantly those of the resin with wood as a reinforcing agent. *The qualities of the plastic predominate.*

Considerable thicknesses of such improved woods are made consisting of large numbers of laminations. Many variations are attained by altering directions of the grain at regular intervals, etc. The illustration (Fig. 105) shows some of the possibilities in this direction.

It has been found that the most suitable thickness of veneer is of the order of one-thirtieth of an inch. The proportion of resin present can be controlled by the thickness of the veneer employed. The use of impregnated paper adhesives is quite straightforward, being merely a matter of cutting paper to size and assembling.

Liquid resins may be used in several ways and involve the more complicated process, e.g. mixing, spreading, and drying. The sheets of veneer may be soaked in phenolic resin solution until completely impregnated for a time which will depend on the thickness, the type of wood, and the rate at which the resin penetrates. Other methods have been used for depositing the resin—

(*a*) immersion of veneer in a solution under vacuum pressure;

(*b*) stacking together partly soaked veneers and allowing the resin to diffuse, etc.

The main object is to make the resin penetrate the cell walls of the wood which are responsible for much of the behaviour of wood, in particular towards moisture. Mere filling up of the cell cavities of the wood does not altogether have the desired effect since the cell walls are still able to shrink or expand by taking up moisture. It has been shown that specially designed resins must be used for these procedures. In these cases the formation of the resin has only been carried through to an early stage, e.g. a water-soluble resin not advanced beyond the phenol-alcohol stage so that the size of the resin molecule is not sufficiently great to prevent penetration into the wood cell walls.

When the veneers have been adequately impregnated, surplus solvent is removed so that no blisters will be formed when the resin is subjected to heat and pressure. Such drying must clearly be carried out at temperatures which will not set the resin. The desired number of impregnated veneers is then assembled and subjected to heat and pressure. In general not more than 30 per cent of resin is used in such production.

It is found that pressures of the order of 1,500 lb. per sq. inch are necessary when using impregnated tissue as the bonding agent. With impregnated veneers, using liquid adhesives on the other hand, lower pressures of the order of 500 lb. per sq. inch are adequate. The usual temperatures, e.g. 140–170°C. are employed.

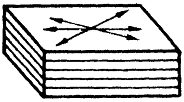
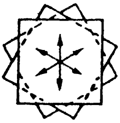
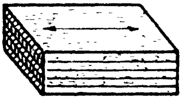
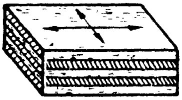
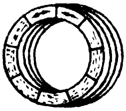
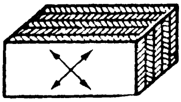
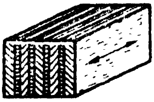
DESCRIPTION.	DIAGRAM	GRAIN STRUCTURE
MATERIAL FOR TRANSMITTING FORCES WHEN SECURED BY CROSS BOLTING E.G TENSILE LINKS		CLEAVAGE IS RESISTED BY A PROPORTION OF GRAIN STRUCTURE BEING INCLINED TO DIRECTION OF STRESS.
MATERIAL FOR GEAR BLANKS OR LOADED WHEELS		GRAIN DISPOSITION APPROXIMATELY EQUAL IN ALL RADIAL DIRECTIONS
MATERIAL FOR MAXIMUM RESISTANCE TO BENDING, TORSIONAL AND TENSILE STRESSES		ALL GRAIN IN DIRECTION OF THE AXIS OF LOAD
MATERIAL TO RESIST COMPRESSION OR TO BE EQUALLY RESISTANT TO STRESSES AT RIGHT ANGLES.		EQUAL PROPORTION OF GRAIN STRUCTURE PARALLEL TO EACH AXIS
SEGMENTAL RINGS.		ALL GRAIN STRUCTURE SUBSTANTIALLY TANGENTIAL TO THE RIM
MATERIAL TO TRANSMIT STRESSES IN TWO DIRECTIONS AT RIGHT ANGLES, THE STRESS BEING TRANSFORMED BY CROSS BOLTING.		MATERIAL AS (6) BUT WITH GRAIN STRUCTURE AT 45° TO AXIS.
RAILTRACK INSULATION.		

Fig. 105. Variations possible by different arrangement of layers[7] (Grades of Permali)

Density of Improved Wood. The density of the materials which may be obtained by these high pressure processes is a matter of some interest and importance. The limits are obviously the ultimate specific gravity of wood which is about 1·55 and the ultimate specific gravity of phenolic resin which is about 1·4. For all practical purposes the top density obtained is about 1·3. By having a lower degree of impregnation and using lower pressures lower densities may be produced.

The density of normal spruce ranges from 0·34 to 0·4; poplar from 0·4 to 0·45; and birch from 0·6 to 0·7. In making compressed wood it is difficult to keep the value below 0·75 and the usual density is about 1. It is of some interest to notice that the density of the dense natural woods such as lignum vitæ and ebony is about 1·25. As a result their desirable characteristics can be reproduced in high density plywood, a matter which is of some importance at the present time.

These impregnated woods may be worked with the aid of special tools on ordinary wood-working machinery, or as if they were mild steel on metal-working equipment. By virtue of their great hardness and toughness they can be assembled with rivets or screws, but they cannot be nailed. They may be glued.

Some of the leading applications of these resin-impregnated, compressed laminated include aeroplane propellers, templates, tools, jigs, fixtures and so on in the aircraft industry. In chemical engineering they are also used for fan blades, bench tops, acid hoods, etc. Ship propellers and railway truck parts are other interesting applications.

Jervis[4] has detailed the following applications:

Uses of Laminated Wood

(*a*) Switch panels
(*b*) Terminal boards
(*c*) Operating poles
(*d*) Fuse handles
(*e*) Lift rods for oil circuit breakers
(*f*) Explosion pots
(*g*) Insular spindles
(*h*) Cross-arms
(*i*) Transformer blocks
(*j*) Winding supports for motors, etc., etc.

Use of Improved Wood for Air Screws, etc. High density improved woods have a very wide application for aircraft purposes. For example, they are used for reinforcing plates giving excellent reinforcement for the attachment of spruce spars. One of the most important applications of improved wood is in the manufacture of air screws. A number of processes have been developed for making these, introducing several ingenious new principles. The conditions which have to be withstood are described by the fact that an aeroplane travelling at high speed imposes a centrifugal force on each blade root of something like 20 tons, where the highest speed of rotation is 900 ft. per second. The stresses imposed decrease down the length of the propeller blade. As a result, the production of variable density wood has come about.

In practice, the veneers are assembled in such a way that the number of veneers decreases along the length of the sheet, while the number of glue lines increases. The pack may have twice as many sheets of veneer at one end as it has at the other end. When this is subjected to heat and pressure, a board of uniform size is obtained, but the density varies according to the number of glue lines. This can then be shaped to propeller form with the densest portion attached to the hub. Such construction supplies a very convenient method of attaining greater strength at the hub than at the tip.

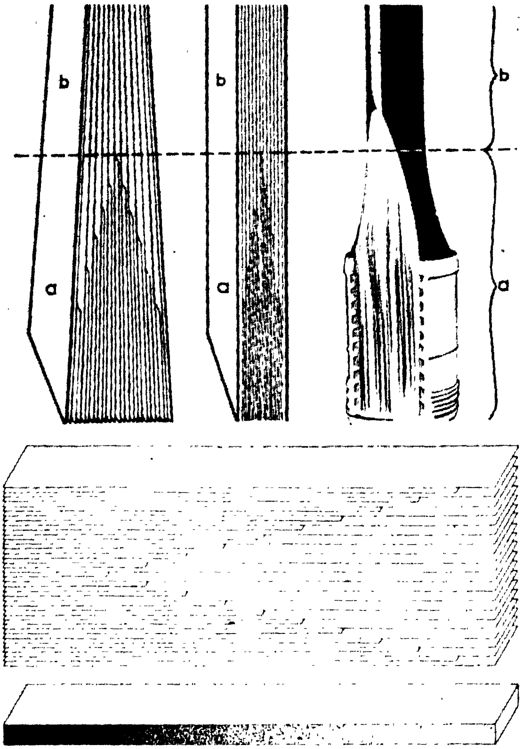


Fig. 106. Constructions used for building compressed wood of varying density[13]

Another type of air screw is made by scarfing $\frac{1}{2}$ inch layers of compressed plywood to spruce so that there is high density material at the hub end giving adequate strength for attachment to the engine. The low density at the outer tip reduces centrifugal force to a minimum.

Another procedure for making air screws from plywood is to trim each sheet of impregnated veneer slightly over its final size and shape, and then to cure the complete assembly under heat and pressure in a metal mould. The air screw blade is pressed to exact shape and twist, leaving a small amount of material to be turned off after the cure. By varying the number of layers of veneer, high density material can be attained to be attached at the hub.

TABLE 72

PHYSICAL PROPERTIES OF USUAL MATERIALS FOR JIGS AND FIXTURES

	Ultimate Tensile Strength, lb./sq. in.	Shearing Stress, lb./sq. in.	Modulus of Elasticity, lb./sq. in.	Specific Gravity	Weight per cub. in.	Brinell Hardness, kg./mm.^{2}
Paper laminated	15,000–19,000	15,000–17,000	1,150,000–1,600,000	1·38	22·6 gm.	30–40
Fabric laminated	8,500–11,000	11,000–13,000	850,000–1,300,000	1·34	22 gm.	30
Cast-iron .	20,000	24,000	12,000,000	7·85	128 gm.	140
Steel machinery	60,000	45,000	30,000,000	7·85	128 gm.	Variable
Aluminium; alloy, cast .	21,000		10,000,000	2·8	46 gm.	85–100
Wood . .	13,000			0·7	11·5 gm.	6·6

Use of Improved Wood for Tools. Improved wood has become extremely valuable to the vast metal-working industries for press tools. It is used for making:

1. Drill Jigs.
2. Routers.
3. Press Tools.
4. Profile Plates.
5. Bending Blocks.
6. Templates.

For small quantity production of cold pressings, i.e. series of up to several thousand articles, these resin-impregnated wooden tools possess several important advantages over standard hardened steel products. Although pound for pound the improved wood is more expensive than the metal, in actual production of tools the wood is more economical, as pattern making, moulding, etc., are eliminated and blocks of the non-metallic material can be machined immediately with ordinary metal working tools. Even wood-working tools are adequate if special working precautions are taken. It is as well to realise, however, that for long runs of many thousands, the wooden press tools are not suitable. In general they fulfil all needs for the numbers required in modern aircraft production.

The average output of an improved wood press forming tool is about 2,000 to 2,500. Even when the tool shows signs of wear it need not be scrapped for it can be built up for re-use.

In the case of hot pressings up to 300°C. a good laminated wood tool should be able to produce runs of 500 to 700 without injury. Wood is not a reasonably homogeneous substance like steel, and uncertain stresses are likely to be set up in the material, which may lead to slight deformation.

Several practical advantages are claimed for these impregnated wood press tools. In the first place, as laminated wood is less than one-fifth the weight of steel, it requires less labour to handle. Another important advantage of the new wooden type of press tool is that, unlike metal, it can be easily modified during production; whereas in the case of steel, changes in design usually entail the ordering of fresh tools. At the present time, large numbers of blanking tools are being made of resin-impregnated wood. In tools of this kind, punch and die are faced with a mild steel plate which provides the cutting edge. In forming tools, also, steel inserts are incorporated in the dies at points where exceptionally heavy wear is to be expected, such as on sharp corners or where severe curvatures are required.

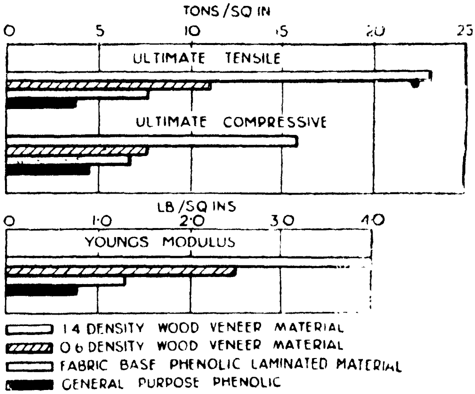


Fig. 107. Comparison of some physical properties[11]

Moulding Plastic-Bonded Wood. The most spectacular application of plywood in recent years has been to aircraft. In a sense this is merely a return to old practice, since plywood construction was widely used at the end of the last war. Departure from this was due largely to the unsatisfactory behaviour of existing adhesives. A number of novel methods have been introduced whereby large shaped structures may be moulded in plywood. Latterly the mass production of small boats has been very impressive.

"Moulded" resin-bonded plywood has equally interesting possibilities in many other industries. The manufacture of resin-bonded car bodies is both technically and economically possible. Furniture construction is also likely to undergo certain changes in design as soon as moulded plywood components become available again.

The continuous lamination of veneers into tubing and ducts by the winding method may produce interesting components for building purposes. Firstly, because ducts and similar tubes could be used for air-conditioning channels, and smaller tubes for the housing of electric conduits. Secondly, certain building components such as framing elements could be produced from laminated tubes by further fabricating processes.

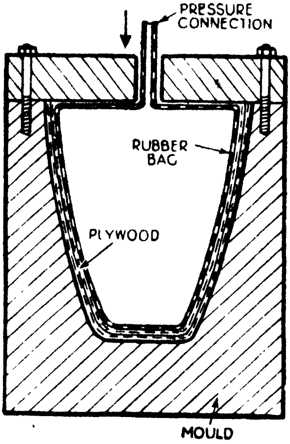


Fig. 108. Completely enclosed forms may be moulded by the internal moulding process shown[13]

Although the aircraft industry has led the way in these developments they have a widespread application throughout many other industries, e.g. shipbuilding, automobiles, building, etc.

Reference to plastic planes is very misleading. It greatly exaggerates the part played by the plastics which are present. In actual practice this type of aircraft is made up of 90 per cent wood and 10 per cent synthetic resins. In the main, the resins have replaced the older types of glues. They have had the effect of speeding up production, giving improved products.

The synthetic resins enter into the aeroplane construction in four ways:

(*a*) In the form of large areas of plywood which is either flat or shaped.
(*b*) In the form of improved wood.
(*c*) As cold bonding adhesives in assembly work.
(*d*) In the construction of tools and jigs, etc.

The use of synthetic resins confer a number of advantages which account for the increasing rate of their application in the aircraft industry. These have been summarised as:

(*a*) They greatly increase the speed of production.
(*b*) They confer a high stiffness per unit of weight about 81 times as great as Dural.
(*c*) They facilitate improved streamlining.

(*d*) They are less expensive and much lighter.
(*e*) They afford much greater ease of fabrication.
(*f*) The machinery required is very simple.

The use of plywood aircraft parts in assemblies confer these numerous advantages. The structures obtained have a high strength weight ratio and they are, moreover, unaffected by moisture, fungi or other deteriorating influences. Panels and structures having the same weight as light metals, have far greater resistance to buckling. The elimination of rivets gives smooth exterior surfaces, thereby reducing any tendency for drag and leading to higher speeds. In general, the materials employed are freely available and can be used by personnel accustomed to working with wood.

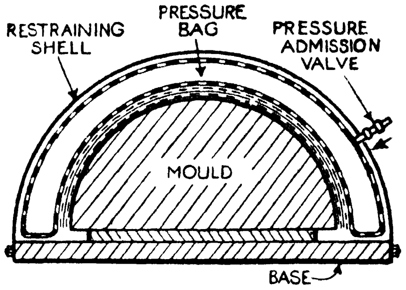


Fig. 109. Moulded plywood construction, using inflated bag with positive pressure[13]

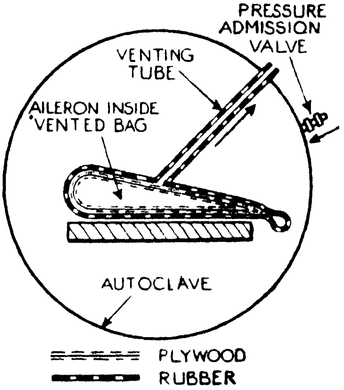


Fig. 110. Deflated bag method, using vacuum pressure[13]

There are some disadvantages. These materials are more inflammable than metals. However, in relation to the imflammability of petrol, this difference is not a matter of great significance. It is also evident that for many structural purposes these materials will not be satisfactory.

Among the leading types of products already prepared for aircraft from plastic bonded laminated wood are the following: laminated spars are made from veneers in which the grain of each sheet runs parallel. There is a tendency to make spars from laminated wood. Almost unlimited lengths can be obtained by applying scarfing methods. The products obtained are superior to solid wood. They are being employed in the construction of trainer planes. A wide variety of plywood ribs and gussets are used for reinforcing purposes.

There is also a strong trend for the use of plywood as skin coverings. Being about one-fifth the weight of aluminium it has obvious advantages from this point of view. Plywood can also be glued to ribs and spars whereas metals have to be riveted. It also has resilience, so that where a metal sheet would be dented by impact, plywood is unaffected.

Moulding of curved sections of plywood bonded with synthetic resins has developed chiefly in the aircraft field. The methods are only possible for large curvatures. The process involves heating the assembly of plywood under pressure. In this way the rapid setting characteristics of synthetic resins are utilised, and enable rapid production. In general the phenolic resins have given most satisfactory results.

The Use of Rubber Bags. The great step in technique which has evolved is the use of a rubber bag as one part of the moulding unit.

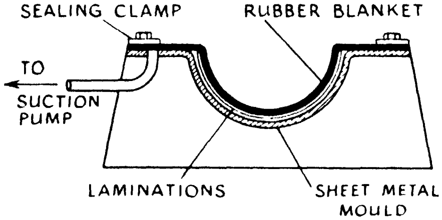


Fig. 111. Duramold method[13]

Pressure applied through a rubber bag is very similar to fluid pressure and therefore acts at right angles to any surface under pressure. Practically all the processes which have been developed for making aircraft parts from plywood in recent years have been based on this principle. One procedure is to have the main mould of metal or wood. This rests on a base plate. An outer cylindrical metal shell is firmly bolted to the base plate. The veneers of wood are assembled on the shaping core. They are located by means of tacks or adhesive tape, etc. A deflated rubber bag is placed over the assembly, the outer shell is dropped over the top, and bolted to the base. The rubber bag is then inflated with air, thus pressing the wood veneers together. Frame members may be inserted into the mould, and these, too, will be bonded.

Vidal Process. Vidal and Marhoeffer[10] have developed a process for the forming of curved sections with veneers. It is described as "cooking wood and plastic into any kind of shape." Up to the present it has been mainly applied to aircraft construction.

The process involves curving the veneers to the required shape over a solid wood form, coating the plies and reinforcements with a thermosetting resin and applying heat and equal pressure to all parts to bond them into a single integral structure.

A solid wood form is first made. For making a fuselage, reinforcing strips and members are required. The corresponding slots to take these must be cut into the wood form. Veneer sheets and strips are cut to templates. They are coated with the requisite resin, and they are then applied to the wood form. This wrapping technique is continually being improved.

When assembled, the plywood has to be subjected to heat and pressure. Fluid pressure is essential in order to obtain equalised pressure. A moisture-proof membrane is essential. Rubber bags have been used, but special bags are now employed which stand up better to the exacting conditions of heat and pressure. The bag enclosing the mould with its superimposed plywood assembly is wheeled into an autoclave. Steam under pressure is admitted. At the same time all air is exhausted from the membrane by a special device. Pressure ranges from 20 to 50 lb. per sq. inch and temperatures from 88°- 150° C. according to the thickness of the job.

Fig. 112. Assembling strips of veneer for moulding a fuselage[12]

After removal, the exterior of the moulding is smoothed. A complete fuselage may then be made by joining two halves longitudinally.

Articles such as aircraft fuselages, wings, floats, skis, and small boats have been made on an impressive scale by this method.

The Duramold Process. In the Duramold[1] process the mould is female and is made from thin sheet metal, such as $\frac{1}{8}$-inch Duralumin sheet, which is highly polished and correspondingly smooth. This sheet is provided on its outer surface with a stiffening framework, which holds it in the required shape but need not be very heavy.

Plywood treated with resin is then fitted in layers into the mould. If necessary the plywood is cut in gore-shaped strips to facilitate placing it, without wrinkles, in areas which have a double curvature; in this case adhesive tape is sometimes used to hold laminations in place until they are bonded by moulding. The number of layers is varied to meet requirements and need not be uniform over the entire area. In fact, it is common to vary the thickness more or less in proportion to the stress or degree of rigidity required, so as to minimise weight.

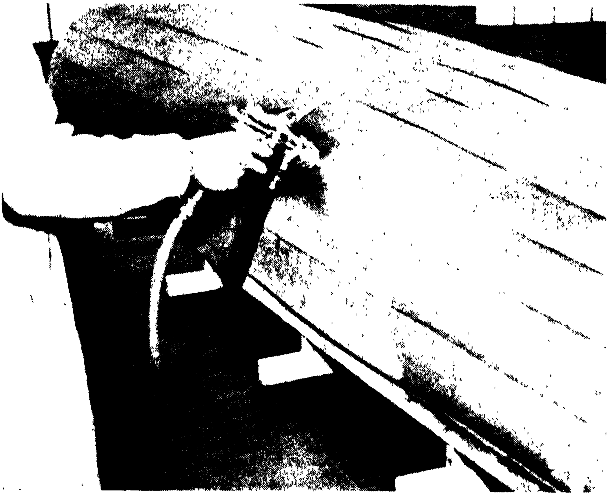


Fig. 113. Resin adhesive being sprayed on prior to adding further layers of veneer[12]

The plywood is then covered with a rubber blanket, and the latter is clamped against the edges of the mould, sealing the charge between the mould surface and the blanket. Temperatures are shown by thermocouples inserted at convenient positions. After the mould is sealed, air is exhausted from it. The mould is placed in an autoclave. Steam is then admitted and creates pressure on both sides of the mould, that is, against the blanket on one side and the sheet metal of the mould on the other side. As the pressure is uniform over the entire surface, it is balanced and there is no tendency to distort the mould.

Pressure is raised to about 100 lb. per sq. inch. The steam has a temperature of about 150° C. and the resin used fluxes at 140° C. maximum, so that the required bond is effected, heat entering the plywood through both the mould and the blanket.

If the moulding formed has a maximum thickness of $\frac{3}{8}$ inch, the time required in the autoclave is about 10 to 12 minutes. It is less for thinner mouldings and greater for thicker, but in all cases the curing continues until the thermocouples show that the required temperatures have been attained in the thickest sections, thus ensuring complete fluxing and firm bonding at all points. The steam is then turned off and the pressure reduced to atmospheric, after which the autoclave is opened and the mould removed, with its charge.

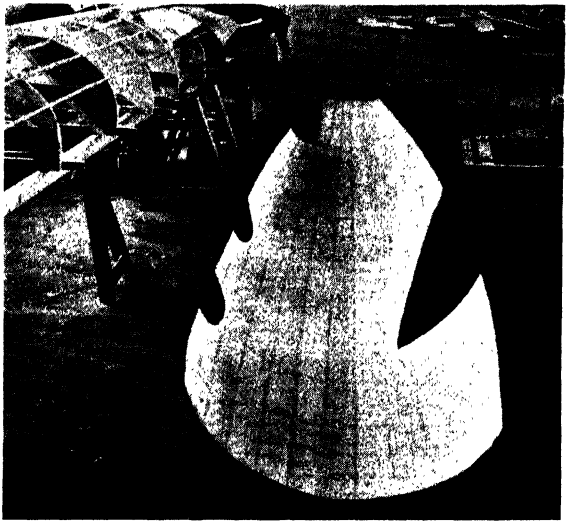


Fig. 114. Timm "Aeromold" Trainer

The finished half of a fuselage shell after coming out of the mould after a short cure under heat and pressure. Notches for cockpit, etc., are cut to template before the shell is assembled on the jig

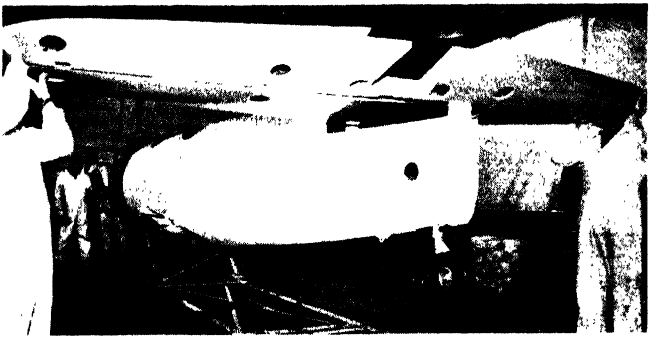


Fig. 115. Attaching resin-bonded plywood tail-planes

Ribs and spars can be built up by similar means. Spars are being fabricated from short lengths of ⅞-inch spruce and from other woods. At the ends of the short lengths, scarf joints are made with phenolic adhesive and a similar joint between the laminations.

Complete wing sections have been fabricated by moulding two halves and assembling them at scarfed joints. It is also possible to assemble ribs to the moulded coverings. This method has been applied to the production of many aircraft.

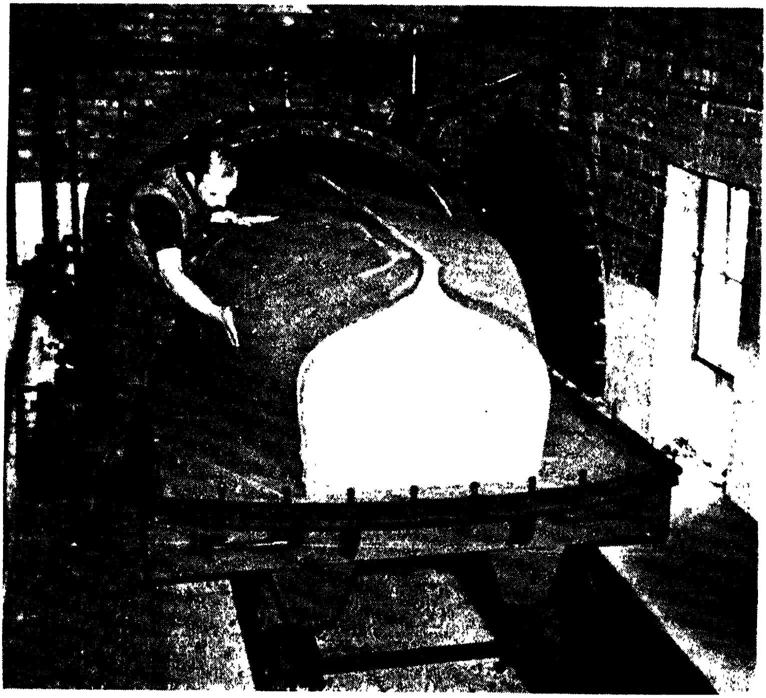


Fig. 116. Boat shell assembled on mould covered with rubber being placed in autoclave[14]

There are a number of other variations on these themes. They are being more and more widely employed and the units which are being made from them become progressively larger. Such items as half a fuselage can be moulded in a few minutes and then two halves may be stuck together.

Application of Laminated Plywood to the Production of Boats, etc. The excellent characteristics of plastic-bonded plywoods have led to wide scale application in the production of boats and small craft of every description on mass production lines. Numerous examples are to be found among the naval craft at the present time. Such boats are being produced on a large scale made with frame stems and engine-bearing parts all constructed from resin-bonded plywood. The frames of all the parts are cut to shape in the factory and are subsequently assembled very rapidly and effectively. The use of plywood for other marine purposes such as frames, bolt heads, decks, etc., as distinct from interior applications is also increasing.

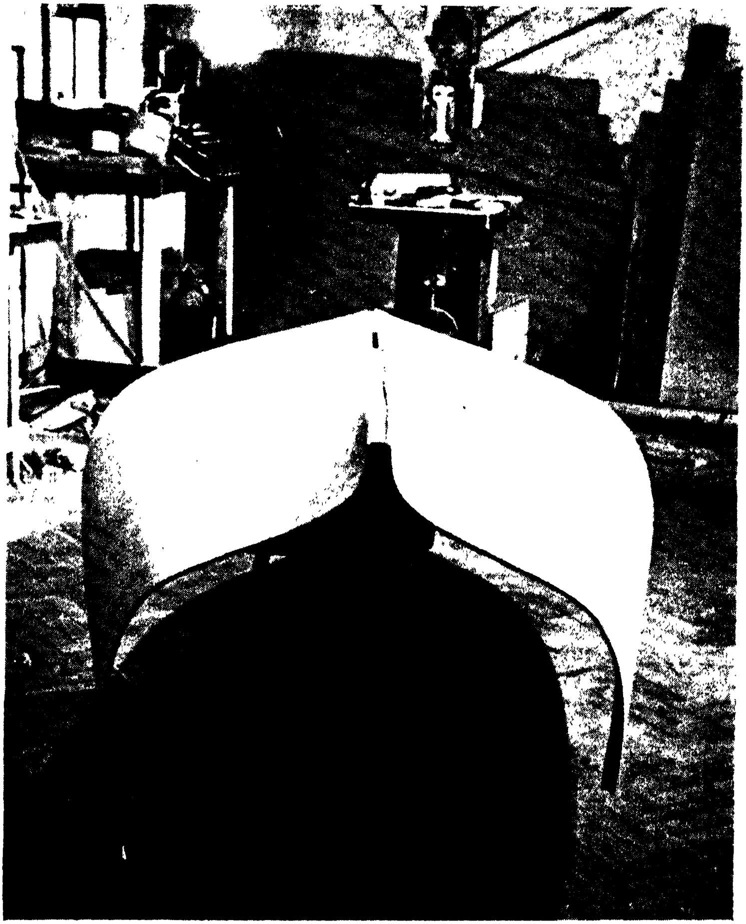


Fig. 117. Finished boat shell removed from mould[14]

Small boats are now moulded[6] from resin-bonded plywood much along the lines followed with aircraft parts.

A mould of the desired form is constructed in wood or metal and suitably perforated to facilitate the production of an internal vacuum.

Slots are cut in the mould to receive any internal bracings which may be required in the ultimate structure—in the case of a boat the keel/hog/stem assembly and the gunwale.

Mahogany veneers are coated with resin, formed into phenol-bonded sheets in a manner which gives them a fabric-like multi-directional pliability and packs of such sheets are then cut into a pattern obtained from a development of the mould surface, in a method not unlike those used in mass-production tailoring.

The interior bracings having been laid in their approximate slots, the patterned sheets are placed on the mould, coated with a special phenol-formaldehyde resin and the desired thickness built up.

When this shell structure is complete the whole is covered with a rubber counter-mould and the complete assembly, which has been made on a trolley running on a rail track, is moved into a large, steam-heated autoclave.

The pressure vessel is closed, vacuum is applied from within the mould, while external pressure (about 50 lb. per sq. inch) is exerted on the face of the assembly, the temperature being maintained at about 80°C.

After a period of about 10 minutes curing is complete and the now completely formed shell is removed.

The boat is finished by fitting on the outside stem, transom and interior thwarts and knees, many of which sections are themselves of resin-bonded laminated construction.

It is evident that these are mere beginnings. The subject is in its infancy. Great strides can be expected when activities may be directed into ordinary channels for the production of ordinary articles. Already such materials are being used to make laminated arches, engineering timbers, bridge trestles, etc. An outstanding commercial production is the large-scale manufacture of barrels.

REFERENCES

1 Duramold. *Plastics*, 1941, **5**, 94.
2 EGNER. *Kunstoffe*, 1941, **37**, 27.
3 GALLAY. *British Plastics*, 1944, **16**, 103.
4 JERVIS. *British Plastics*, 1943, **15**, 223.
5 LIVINGSTON SMITH. *British Plastics*, 1943, **15**, 391.
6 Merron, Ltd. *Plastics*, 1941, **5**, 196.
7 Permali. Technical Literature of New Gloucester Insulation Co., Ltd.
8 PERRY. *Plastics*, 1943, **7**, 123; "*Modern Plywood*," Pitmans, New York, 1942.
9 Tegofilm. Technical Literature of Micanite and Insulators, Ltd.
10 VIDAL AND MARHOEFFER. U.S.P. 2,276,004/1942.
11 WARBURTON-BROWN. *Plastics*, 1943, **7**, 3.
12 Illustrations by courtesy of *British Plastics*.
13 ,, ,, *Flight*.
14 ,, ,, *Plastics*.

PART III

CELLULOSE PLASTICS

CHAPTER XIII

GENERAL CONSIDERATIONS

THE plastics based on cellulose constitute one of the oldest established and most important groups in the industry. They are the leading thermoplastic materials. In volume their use far exceeds any other thermoplastic at the present time. Among them they cover a very wide range of properties which make them suitable for numerous diverse applications. Thus in 1948 over 2,000 million lbs. cotton linters were used in making cellulose derivatives including rayon.

Cotton linters are subjected to careful chemical treatment for conversion into cotton cellulose. For many purposes it is necessary to remove the particles of hulls which remain after the removal of long staple cotton. In the final product the cotton cellulose is usually dried into sheets which look like blotting-paper. They are transported in this form for the production of viscose, for explosives, for paper, and for cellulose plastics.

The behaviour of cellulose is judged by the viscosity of standard amounts in cuprammonium solution. The following table shows a typical analysis of chemical cotton:

TABLE 73

α-Cellulose	94·00
Ash	0·10
Ether soluble	0·20
Lignin	0·20
Iron	0·002
Moisture	5·5

The leading materials which have attained commercial importance include the esters comprising cellulose acetate, nitro-cellulose (or cellulose nitrate), cellulose acetobutyrate, and cellulose acetopropionate. Apart from these there are the cellulose ethers, the chief members of which are ethyl cellulose and benzyl cellulose. The latter has not so far justified the high hopes held out for it.

Cellulose Derivatives are not Synthetic Resins. These materials differ fundamentally from most of the other synthetic products coming in the purview of plastics. They are not synthetic resins; they are synthetic materials only in the sense that a natural product has been taken and modified by chemical methods. The large complex molecular structure, which is an essential feature of plastic materials generally, has in this instance not been built up by chemical methods. Cellulose itself already has such a complex large molecule built up by nature. This is the significant factor which accounts for the outstanding physical properties of cellulose products. In a sense this is comparable with the long molecule of rubber—another natural long chain material.

In the treatment of cellulose to produce plastic materials, the chemist has modified the portions tacked on to the main structure. Nevertheless, this in itself has had very profound effects on the behaviour of the materials. The other modification which synthetic chemistry is able to achieve is by reduction of the length of chain. Likewise this is a process comparable with that carried out on rubber.

TABLE 74

DEGREE OF POLYMERISATION OF CELLULOSE DERIVATIVES

	Staudinger	Kraemer
Nitro-cellulose (cotton, ramie, flax)	2,000–3,000	3,500
Commercial wood pulp	800–1,000	600–1,000
Purified wood pulp	900–1,500	—
Cotton linters—purified	—	1,000–3,000
Commercial Regenerated Cellulose	250–500	200–600
Nitro-cellulose (dynamite)	2,000–3,000	3,000–3,500
Nitro-cellulose (plastics)	—	500–600
Nitro-cellulose (lacquer)	300–600	175
Commercial Cellulose acetate	200–350	175–360
Commercial Ethyl Cellulose	200–500	—

Staudinger—Viscosity methods.
Kraemer—Ultra-centrifuge methods.

The length of the chain in pure cellulose, according to Kraemer[6] and Staudinger[9] is between 2,000 and 3,000 glucose units. These cellulose chains form different larger groupings or micelles sometimes associated with the materials which accounts for the various species of cellulose products, e.g. cotton linters, wood pulp, ramie, straws, etc.

According to Yarsley and Couzens[10] "The application of X-ray analysis to cellulose shows that it is built up of bundles of long chains . . . each bundle or 'micelle' containing less than a hundred chains. . . . The X-ray analysis of cellulose plastics gives some confirmation of the existence of a similar pattern."

Cellulose has a long chain molecule which can be modified by internal substitution. Cellulose is generally accepted as having a chain-like structure which is transmitted to its derivatives. These molecules, each consisting of a long chain, are loosely interlaced one with the other, and both their length and interlacing arrangement impart to cellulose good mechanical strength, toughness and stability. It is precisely this long thread-like structure which is considered to impart to cellulose and its derivatives toughness, flexibility, the ability to form films, and the ability to form fibres. The high molecular weight of these chains are leading factors in contributing to the important physical characteristics of these materials. In general cellulose derivatives have exceptional strength accompanied by toughness and flexibility.

All the cellulose derivatives have relatively high softening points which make them difficult materials to handle alone without any modification. It is therefore necessary to add agents which will accentuate and bring out the desirable plastic characteristics, so as to make them workable by available methods. These objects are achieved by the addition of modifying agents known as *plasticisers*. The development of plasticisers has largely been bound up with the evolution of cellulose derivatives as plastics.

The Cellulose Molecule and its Behaviour. It is generally accepted that the cellulose molecule is built up of a large number of glucose units linked together by oxygen bridges. This conception first envisaged by Hawarth,[4] finds wide acceptance because it is able to account for much of the behaviour of cellulose and its derivatives.

According to this long chain conception of cellulose each glucose unit contains three hydroxyl groups. Two hydroxyl groups are secondary, whereas the one on carbon atom No. 6 is primary. These hydroxyl groups are reactive and subject to chemical changes, along the lines of ordinary alcohols, i.e. favouring formation of esters and ethers. The whole series of esters and ethers may be prepared by chemical reactions based on these hydroxyl groupings. Treatment with nitric acid, for example, in the presence of sulphuric acid, yields cellulose nitrate. Treatment of acetic anhydride and acetic acid results in the formation of cellulose acetate; and so on. On the other hand, treatment with ethyl chloride leads to ethyl cellulose, and with benzyl chloride results in benzyl cellulose.

All these chemical changes can take place without affecting the long chain structure which remains intact. The chief change is the difference in intensity with which each cellulose chain is attracted to its neighbours.[5]

The conditions under which the treatment is carried out have a profound influence on the properties of the products. The long thread-like molecules are disrupted under the influence of excessive heat or mechanical treatment, etc. Shorter chains are formed. There is a corresponding influence on solubility and on properties such as viscosity. The degree of polymerisation of cellulose derivatives has been the subject of much study. Table 75 shows results which have been obtained.

TABLE 75

RELATIVE FILM AREA OF CELLULOSE DERIVATIVES

Material	Specific Gravity	Area of Film 1/1000″ thick in sq. in. per lb.
Ethyl Cellulose	1·13	25,000
Benzyl Cellulose	1·17	23,700
Cellulose Acetobutyrate	1·22	22,700
Cellulose Acetopropionate	1·25	22,200
Cellulose Acetate	1·37	20,200
Cellulose Nitrate	1·65	16,800

The nature of the chemical changes and the amount of the new groups introduced leads to the production of a large number of different products having widely varying characteristics. It should be made quite clear that the commercial success of cellulose plastics depends largely on the supply and price of such heavy chemicals as nitric acid, sulphuric acid, acetic acid, and also of synthetic chemicals such as ethyl chloride, etc. These are used in large quantities, and very often the efficiency of recovery of such chemicals determines and dominates the commercial status of the plastic.

The classification of the products obtained is generally based on the number or percentage of hydroxyl groups which have been substituted. An enormous amount of work has been carried out in this field, but comparatively few products have been found to possess the range of properties suitable for commercial development. The most critical characteristic which is affected by the various substitutions is the solubility in solvents, and this has been the basis of much of the work carried out. For example, in the preparation of cellulose acetate the triester was found to be insoluble in commercial solvents and consequently its applications have been limited. By contrast, when acetates with a lower degree of substitution were developed, which were found to be more easily soluble, the industrial scope expanded beyond all measure. The wide range of solubility obtainable with cellulose ethers has likewise accounted for the growing applications in recent years.[11]

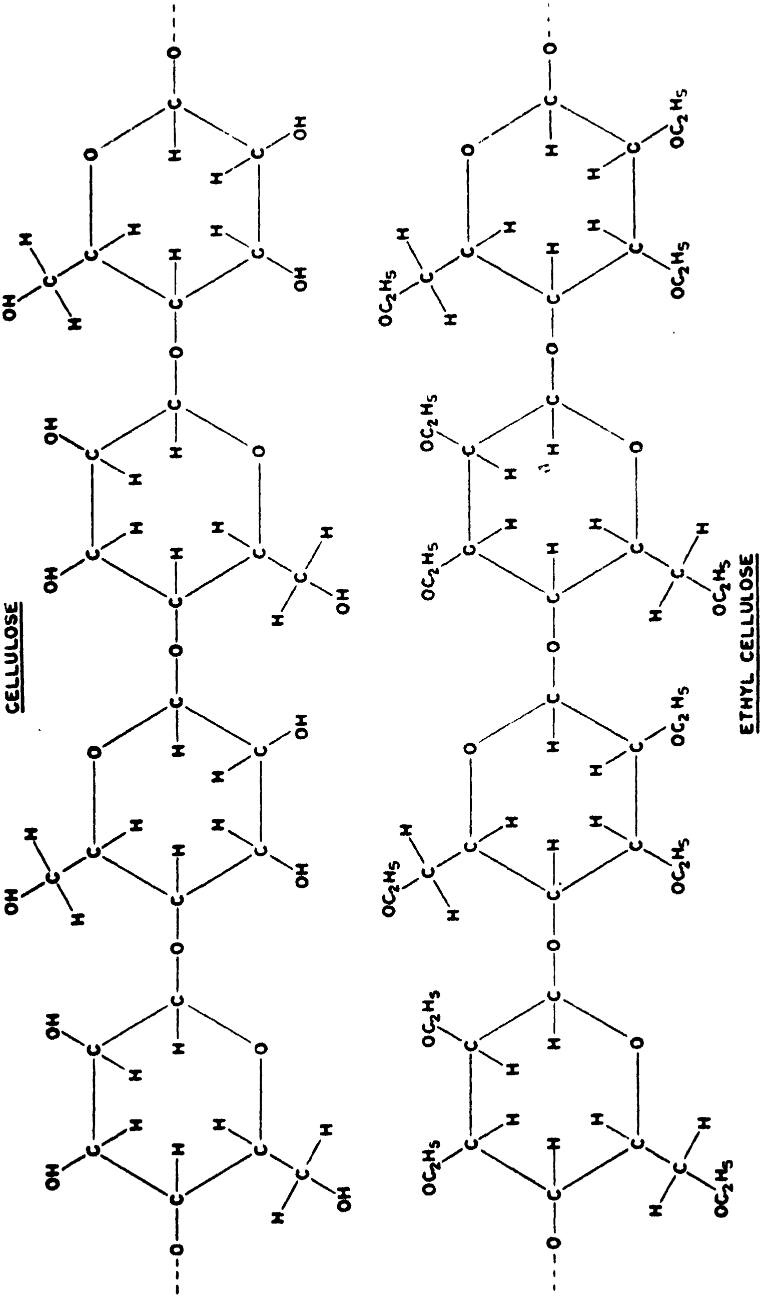


Fig. 118

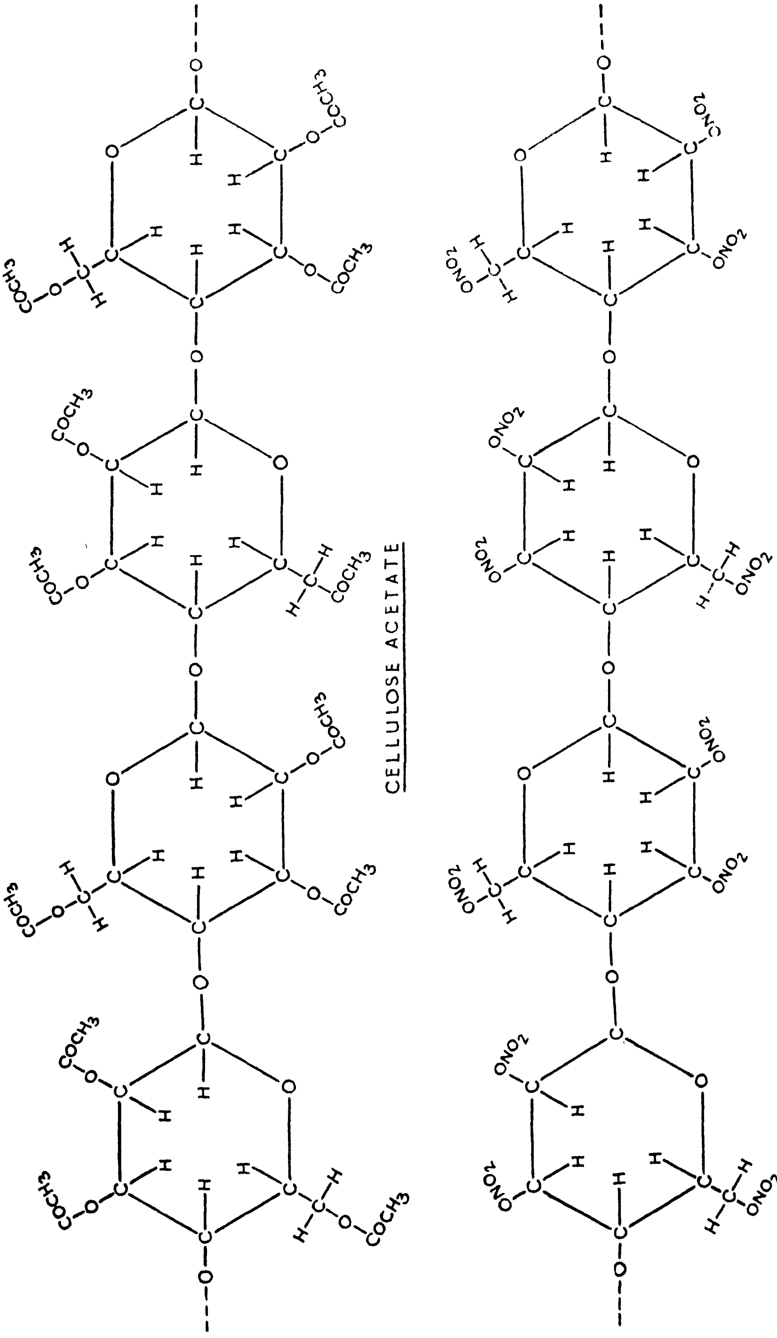
The average chain length of cellulose acetate, according to Kraemer, is between 175 to 350 glucose units.

The glucose units in the cellulose chain are considered to exist as fairly rigid lengths. The lengths are joined together in the chain by oxygen bridges exerting primary valency forces. There is considerable steric hindrance around the oxygen bridges which impedes much movement. One can therefore visualise that the molecules of cellulose and its derivatives form long extended chains which have not a great deal of freedom of movement because the chains are interlocked and each chain has very little flexibility. Both toughness and rigidity of cellulose plastics appear to be explained by this structure of cellulose.

In the picture of the cellulose molecule made up of long chains of glucose units, each unit contains three reactive groups which can be substituted. The chain would be approximately of the same size. The degree of substitution is expressed by the number of hydroxyl groups replaced. A derivative with all the hydroxyls reacted would have the maximum substitution of 3. If the cellulose derivative has an average of 2·5 of the hydroxyl groups reacted, then the substitution is said to be 2·5. Another method of describing the substitution is the statement of the percentage of acetic acid present in cellulose acetate, i.e. the acetyl value; or the percentage of ethoxyl present in ethyl cellulose. In the case of nitro-cellulose it is designated by the percentage of nitrogen present. A great amount of information has correlated the influence of the nature and amount of the substituent material on the properties of the product.

The cellulose plastics used commercially for moulding are prepared from the following four types: high acetyl cellulose acetate having an acetyl content (as acetic acid) of 56 to 58 per cent; normal acetyl cellulose acetate having an acetyl content (as acetic acid) of 52·5 to 54 per cent; cellulose acetobutyrate having a butyryl content (as butyric acid) of 36 to 37 per cent and acetyl content (as acetic acid) of 13 to 14 per cent; ethyl cellulose having an ethoxyl content of 45 to 48·5 per cent.

Nearly all the higher aliphatic esters of cellulose have been prepared. As the acid grouping becomes larger, softening temperature decreases and water absorption decreases. The materials also become progressively weaker. For example, films made from cellulose triester, show that the tensile strength becomes less and elongation greater as the size of the substituent molecule increases. Shepherd and Newsome[8] have measured the variation in properties of triesters containing groups which range from the relatively small acetate to the relatively large



CELLULOSE ACETATE

CELLULOSE NITRATE

Fig. 119

myristate. They found melting point and moisture absorption decreasing steadily as the number of carbon atoms increased.

The properties of ethyl cellulose likewise vary with the ethoxyl content. Lorand[7] found that the softening point of ethyl cellulose is least at extremes of ethoxyl content. A similar state of affairs applies for benzyl cellulose. This shows the effect of a change in the nature of the substituent group on the softening point in the case of ethers. The moisture absorption was found to decrease directly according to the increase in the ethoxyl content. This type of work illustrates very well the variation in properties that can be obtained by altering the nature or amount of the substituent group introduced into the cellulose molecule.

One explanation of the difference in the physical properties of cellulose derivatives according to the degree and type of substitution depends on the forces of attraction existing between the molecules. Two long thread-like molecules in close proximity exert attractive forces on each other. If the small hydroxyl group is replaced by a large grouping, clearly the main chains become separated by a much greater distance. This means that the derivative would tend to become more soluble when the degree of substitution increased.

On the other hand as the degree of substitution increases to a maximum there will be a greater area of contact between adjoining chains. Therefore, it seems probable that the most soluble types will have a substitution less than the maximum. This is found to be the case with most cellulose derivatives where solubility is the greatest between 2–2·5, decreasing once again as it goes up to the maximum of 3.

TABLE 76

WATER ABSORPTION OF CELLULOSE DERIVATIVES AS CLEAR FILMS

	Water Absorption 80% Relative Humidity	Permeability of Water Vapour gm./cm.^{2}/ 1/100 cm./hour
Nitro-cellulose	1·0%	$2{\cdot}8\times10^{-4}$
Cellulose Acetate	4·9%	$8{\cdot}4\times10^{-4}$
Cellulose Acetopropionate	1·0%	$6{\cdot}2\times10^{-4}$
Cellulose Acetobutyrate	1·5%	$7{\cdot}3\times10^{-4}$
Ethyl Cellulose	2·0%	$6{\cdot}4\times10^{-4}$

Comparatively recently a number of mixed esters have appeared as commercial materials.[3] Cellulose acetopropionate, and cellulose acetobutyrate are outstanding types. The materials are not new, having been described, for example, by Cross and Bevan[2] in 1906. The properties of such mixtures vary widely according to the nature of constituents and the proportions present. But the mixtures are soluble in acetone and do not require ripening.

They are made generally by two methods. Direct esterification with mixtures of acid anhydrides is one process; the other is a two-step procedure, esterifying partially with one acid, then finishing off with the other.

The most critical feature of cellulose derivatives is the water absorption and general behaviour towards moisture. It is found that the nature of the substituent has a profound influence on these properties. Cellulose acetate in particular suffers from what is regarded as an excessive water absorption. The properties of the straight cellulose derivatives is shown in the Table 76.

Addition of suitable plasticisers has a profound influence on the behaviour of cellulose plastics towards water.

REFERENCES

1 Cross and Bevan. *Ber.*, 1893, **26**, 1090.
2 Cross and Bevan. *Researches on Cellulose*, Longman's, 1906, p. 90.
3 Hagedorn and Möller. *Cellulose Chem.*, 1931, **12**, 29.
4 Haworth, Charlton and Peat. *J.C.S.*, 1926, **124**, 89.
5 Haworth. *Chem. and Ind.*, 1939, **58**, 923.
6 Kraemer and Lansing. *J. Phys. Chem.*, 1935, **39**, 153.
7 Lorand. *Ind. Eng. Chem.*, 1938, **50**, 527.
8 Shepherd and Newsome. *J. Phys. Chem.*, 1935, **39**, 143.
9 Staudinger, Papier-fabr., 1938, **36**, 385.
10 Yarsley and Couzens. *Plastics*—Pelican Book, 1942, p. 32.
11 Worden. *Technology of Cellulose Ethers*, Vol. 1, p. 7. Newark, 1933.

CHAPTER XIV

NITRO-CELLULOSE OR CELLULOSE NITRATE

CELLULOSE Nitrate or Nitro-Cellulose (the terms are interchangeable) is the basis of the oldest synthetic plastic material. Suitably plasticised, the material known as celluloid, "Xylonite,"[16] etc., is obtained. Celluloid is almost a generic term for nitro-cellulose plastics. In spite of several serious disadvantages, nitro-cellulose plastics have maintained a leading position from 1870 up to the present time. They have played a great part in modern life, perhaps most directly as photographic film base, as numerous celluloid moulded articles, and as cellulose lacquer. Even as gun cotton it is used in the form of a plastic. In recent years cellulose nitrate has been losing ground to other plastics, but still maintains a considerable output.

Celluloid has many extremely attractive attributes, colour, finish, ease of handling and fabrication being among them. Its most distinctive property is the unequalled toughness and impact strength. It is also a comparatively cheap material. Ever since its introduction, efforts have been made to overcome the serious fire hazard due to its inflammability. Although this has been reduced, yet the problem never has been satisfactorily solved. This defect is the principle driving force which has enabled other plastics to replace celluloid for many leading applications.

Recently cellulose nitrate has been plasticised with chlorinated plasticisers to such good effect that the inflammability hazard has been profoundly reduced, thereby enabling the material to be moulded by compression and injection. It appears that this may lead to a considerable expansion in the use of nitro-cellulose, especially in view of its low cost.

The manufacture of celluloid is an industry which is carried out on a large scale in every industrial country in the world. It is part of the manufacture of raw material for gun cotton, and for cellulose lacquers. There are large industries in the United States, in Germany, in Japan, in Great Britain, etc.

The figures in Table 77 illustrate the dimensions of the industry in the United States. It is estimated that world production is of the order of 50,000 tons per annum.

Historical Background. The development of celluloid naturally followed the discovery of nitro-cellulose. Schönbein[12] appears to have

TABLE 77

U.S. CONSUMPTION OF CELLULOSE NITRATE FOR PLASTICS[14]

1923	27,700,000
1937	18,100,000
1939	13,373,000
1940	11,915,000
1941	16,497,000
1946	18,161,000
1947	12,600,000

been the first to make nitro-cellulose as gun cotton by soaking the cotton wool in concentrated nitric acid, washing it, and drying. Examination of transparent specimens by Faraday and Poggendorf[11] led the latter to forecast the future use of the material in windows. Some years later, in 1861, Russell found that the solution of nitro-cellulose in a mixture of ether and alcohol yielded a dope which was called "collodion," which attained some importance for surgical purposes.

However, the first real step forward in the use of nitro-cellulose as a plastic material was made by that very versatile technician of the middle nineteenth century—Parkes.[9] He became interested in nitro-cellulose and carried the subject well forward. He made numerous solutions and products based on nitro-cellulose, in particular studying the possibility of reducing the flammability. He used ammonium and magnesium phosphates, zinc chloride, sodium tungstate among other materials. He also considered the prospect of using nitro-cellulose as insulating material. In 1864 he found that addition of camphor to collodion solution showed interesting results, but he did not pursue the discovery.

The real commercial arrival of celluloid came about through a somewhat odd set of circumstances. A shortage of elephant tusks led to a corresponding shortage in the supply of billiard balls in the United States. As a consequence a newspaper put up a prize of ten thousand dollars for the inventor who could make the most successful billiard ball. The winner of the competition was Hyatt,[5] who produced a perfectly satisfactory product by using nitro-cellulose. The plastic material he called celluloid. His first product was a plastic core based on a natural gum or resin covered with nitro-cellulose applied from solution. Subsequently he patented a mixture of nitro-cellulose and camphor which were mixed together dry by grinding together under heat and pressure. The consequence of this activity was that Hyatt commenced the commercial production of a variety of articles based on these materials which rapidly became a very large business. It is interesting to notice that Hyatt subsequently was responsible for the invention of roller bearings with which his name is more familiarly associated.

In Great Britain following along the lines initially developed by Parkes, the British Xylonite Company pioneered the production in 1877. The work of Spill was also outstanding in these early times, and he was notable for the development of imitation tortoiseshell effects by the use of nitro-cellulose compositions.[11]

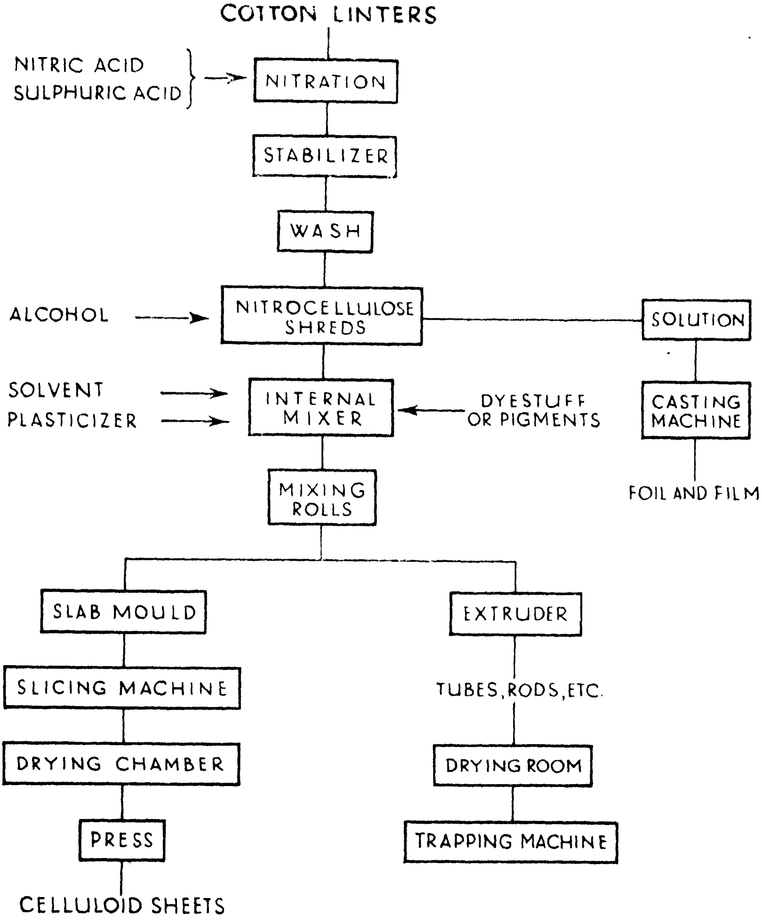


Fig. 120. Flow sheet for nitro-cellulose plastics

Celluloid, even to the present time, consists of nitro-cellulose plasticised almost exclusively with camphor. No other material has been found to exert anything like the same influence as does camphor.

It is an outstanding example of the inexplicable behaviour of a specific material. Many efforts have been made to replace camphor, which at various times has been either in short supply, or unobtainable, but all to no effect. A large synthetic camphor industry has been built up to meet the requirements. Tricresyl phosphate and castor oil are the only other materials having any similar effect.

According to Kraemer,[7] cellulose nitrate for explosives has molecular length or degree of polymerisation of the order of 3,000 glucose units; the plastics type between 500–600 glucose units; while the lacquer type about 175 glucose units.

The Preparation of Nitro-Cellulose. Nitro-cellulose is prepared from cotton linters by the action of concentrated nitric acid in the presence of sulphuric acid as a catalyst.[8] Sulphuric acid serves as a dehydrating agent and also hydrolyses the cellulose.

The chemical reaction involved may be written as:

$$xC_6H_7O_2(OH)_3 + 3x\ HNO_3 \longrightarrow (C_6H_7O_2\,(ONO_2)_3)x + 3x\ H_2O.$$

It is actually much more complex. The extent of reaction is altered appreciably by variation in the composition of the nitrating acid. Nitrating acid is a mixture of nitric acid and sulphuric acid.

Operations involved in production are:

(*a*) Conditioning the cellulose.
(*b*) Preparing the nitrating acid.
(*c*) Esterification.
(*d*) Removing spent acid.
(*e*) Stabilization.
(*f*) Dehydration.

The process is a very sensitive one in which the equilibrium is shifted by small changes in reaction conditions. It is absolutely essential that the cotton linters should be quite dry. The reaction has to be carefully controlled owing to the fact that a number of forms of nitro-cellulose can be obtained having a different nitrogen content depending upon the conditions which are used. Application of the nitro-cellulose depends on the nitrogen content. Theoretically cellulose mononitrate contains 6·77 per cent nitrogen, cellulose dinitrate has 11·16 per cent nitrogen and cellulose trinitrate has 14·16 per cent nitrogen. The nitrogen content of between 10·5 to 11 per cent is the only type really suitable for the preparation of plastics. Above this nitrogen value the material is too inflammable and expensive; it comes into the field of gun cotton. Below the 10·5 per cent nitrogen content the nitro-cellulose is more suitable for lacquers.

TABLE 78

DIFFERENT FORMS OF NITRO-CELLULOSE

Nitrogen Content	Leading Applications
12·2–13·8%	Sporting Powders, Explosives
11·5–12·2%	Lacquers
11·2–11·7%	Films, Rayon
10·5–11·5%	Celluloid

One of the most important properties of cellulose nitrate is the viscosity in solutions. The method of production has a profound influence on this. It can be varied by three methods:

(*a*) Controlling viscosity of original cellulose,
(*b*) Choosing suitable nitrating conditions,
(*c*) By submitting the cellulose nitrate to mechanical treatment, heat treatment, or treatment with dilute acids or alkalis.

Clearly alteration of the two variables—nitrogen content and viscosity gives unlimited scope to the range of types available.

The cotton linters or the alternative form of raw material—cotton tissue obtained from specially selected cotton rags—are carefully dried prior to treatment. They are then treated with mixed sulphuric and nitric acid under carefully controlled conditions. Special equipment is required. The weighed charge of dried linters is placed in a dipping vessel with the requisite amount of mixed acids. The dipper is a non-corrosive steel pot. Each dipper is totally enclosed to prevent fumes escaping. It is also equipped with a stirrer.[10]

A typical procedure is to place 127 lb. of mixed acid in the dipper at a definite temperature, generally about 180°C. 4½ lb. of dried linters are added slowly to the acid. The temperature rises and then slowly returns to the original. The make-up of the mixed acid will depend on the type of the product which is being prepared. It is somewhat empirical in its preparation. For example, one type used for making nitro-cellulose suitable for plastics might contain:

75·5 per cent sulphuric acid
15·75 per cent nitric acid
9·25 per cent water

A typical German production employs an acid composition:

Nitric Acid	21%
Sulphuric Acid	61%
Water	18%

The ratio of acid to cellulose is 50:1. Nitrating temperature is held at 20° C. The product has a nitrogen value of 10·9 per cent. And consumption is found to be 135 lb. of each nitric and sulphuric acid for every 100 lb. nitro-cellulose.

After nitration has been carried through, the dipper is emptied into a centrifuge and excess acid is removed and brought up to strength and re-used. The nitro-cellulose is dropped into a large tank of cold water when most of the remaining acid is removed. The nitro-cellulose is then further washed a number of times until all traces of adhering acid have gone.

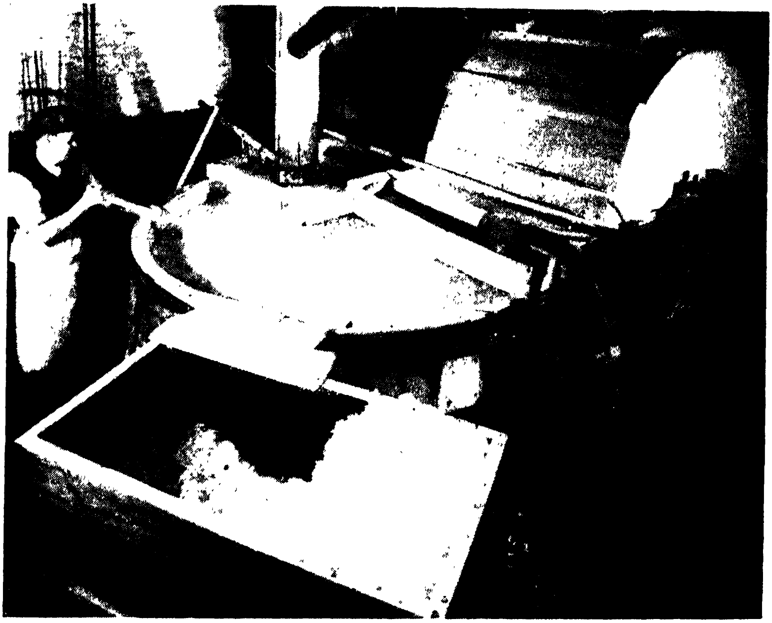


Fig. 121. Mechanical washing of nitro-cellulose[17]

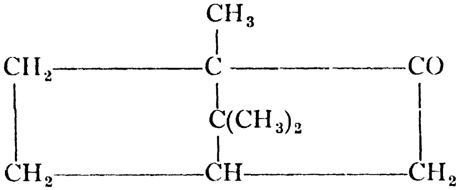
The nitro-cellulose is given a further treatment with boiling water which removes any small traces of acid and deleterious products which may be present and thereby has a profound stabilising influence on the material. This treatment is very important, for a certain amount of acidic sulphate esters are formed which, if not removed, make the material unstable.

The nitro-cellulose is then bleached and once again washed, and then remains as a mass containing a large proportion of water. The water must be removed, and this is carried out by displacing it with alcohol or butyl alcohol in a centrifuge. The resulting product, a white porous material, is the commercial material, which reaches the market containing about 33 per cent of alcohol. It is then ready to be converted into a plastic material. Recovery of spent acid is a very important feature of nitration processes.

Camphor. Nearly all types of plasticisers are compatible with nitrocellulose. But none is so effective as the originally successful material—camphor. Until recent years camphor was obtained exclusively from the camphor tree which grows in Japan, Formosa, and China. It was virtually a Japanese monopoly. Camphor wood is digested with water when camphor and camphor oil sublime with the steam. Camphor is purified by subliming. It is a colourless transparent material with pungent odour. The density is 0·922. It melts at 175°C,. and boils at 209°C. It is used on an extensive scale, not only for celluloid plastics, but also for explosives and for therapeutic purposes.

Adequate supplies of camphor are now made synthetically in the United States, in Germany, and in Great Britain. It is synthesised from pinene which is obtained easily from turpentine. The procedure is:

$$\text{pinene} \longrightarrow \text{bornyl chloride} \longrightarrow \text{isobornyl acetate} \longrightarrow \text{isoborneol} \xrightarrow{\text{oxidation}} \text{camphor}$$



Camphor

At a fairly early stage tricresyl phosphate was introduced as a substitute for camphor. It had the appeal that it reduced the inflammability. On the other hand it is discoloured readily by sunlight—a great disadvantage for transparent requirements. In turn dibutyl phthalate came into use, but it is rather too volatile, so that camphor is still the leading plasticiser for nitro-cellulose—although castor oil is used for such applications as leather cloth.

Preparation of Celluloid. This is in effect carried out by kneading nitro-cellulose with camphor and alcohol in an internal mixer.

The usual proportions which are mixed may be:

100 parts nitro-cellulose
30–40 parts camphor
80 parts alcohol . . .

Where very flexible products are to be produced the higher proportion of camphor is present. Where extremely tough, less flexible products are wanted, the lower proportion is used.

The nitro-cellulose is plasticised or gelatinised by the camphor. In spite of great chemical developments in recent years the use of nitro-cellulose for making plastics is still dependent on camphor. No other known plasticiser or combination of plasticisers approaches it for effectiveness. The process is carried out in a Baker Perkins type of machine or any other type of heavy dough mixer. A temperature of about 30°C. is maintained, and the procedure takes an hour for completion.

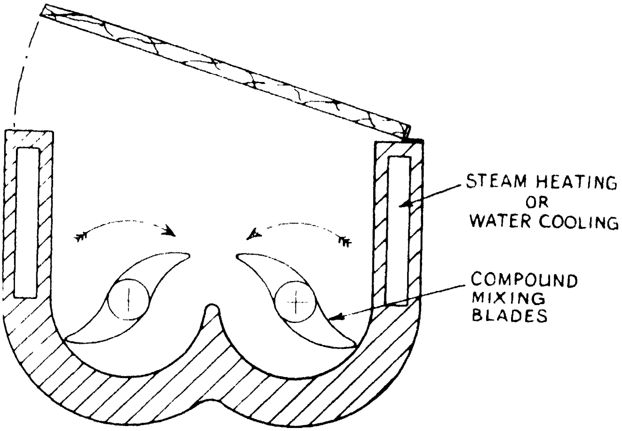


Fig. 122. Cross-section of internal mixer

When the plasticising action has been carried through, the white powdery nitro-cellulose has become a light yellow transparent dough. Where transparent products are to be prepared, the material is used in this form. On the other hand, if coloured products are being made the pigments and dyestuffs are also added during the kneading process.

The internal mixer employed is totally enclosed, so that alcohol which is evaporated during the mixing process may be drawn into a solvent recovery plant and fully recovered. This is an essential feature of the process.

Solvent-laden air is often recovered by the use of active carbon. In this solvent-laden air is blown through layers of special carbon which absorb and retain the solvent, stripping it from the air. The solvent is recovered from the carbon by blowing in steam. It is then condensed, redistilled, and is ready for use once again. Efficiency of the process is of the order of 90 per cent.

Celluloid is available in a wide variety of transparent colours, which are made by the addition of soluble dyes. The use of solid pigments results in the production of opaque materials. The wide range of colours in which celluloid is produced may be prepared in this manner.

Fig. 123. Removing cellulose plastic dough from the internal mixer[17]

The dough is thereafter filtered in order to remove any particles which may be present. This is very necessary where transparent materials or light-coloured materials are being produced. The process is carried out in a filter press under a pressure of 3 tons per sq. inch, through fabric-filter pads.

Preparation of Sheet. Celluloid is generally required for fabrication in the sheet form, so that production is carried through with this object in view. The dough is converted into sheets of celluloid along the following lines.

After being filtered, it is transferred on to hot mixing rolls. The dough is mixed on these rolls for some considerable time, during which surplus alcohol passes off and is drawn away through hoods for recovery. A thick blanket of celluloid forms round one roller and gradually hardens up during the mixing process, as the solvent passes off. When it has reached the desired texture it is transferred to a sheeting mill and rolled off about one inch thick. Special effects are obtained at this stage. Thus tortoiseshell celluloid is obtained by mixing brown and clear plastic materials on the sheeting mill.

Fig. 124. Strings of dough as it comes from the hydraulic filter press as used for celluloid and cellulose acetate[17]

Slabs are cut from the sheets and are then piled into a large steel block mould fixed between the platens of a hydraulic press. The block as made at one concern is 55 × 24 × 6 in. deep. The block mould stands on a removable steel sheet. When the mould is full, the slabs of celluloid are subjected to heat and pressure, until they consolidate to a homogeneous block. A temperature of about 90° C. is used and pressure of 500 lb. per sq. inch. The pressure is maintained for some hours and then the block is cooled off.

There is then obtained a large block of celluloid mounted on a steel base-plate. This assembly is transferred to a slicing machine. The block is fitted on to the movable base, which moves backwards and forwards against a fixed knife. The knife automatically drops the requisite distance after each cut. Sheets of any desired thickness down to five-thousandths of an inch are cut.

These sheets still contain a certain amount of solvent which must be removed. They are hung in warm drying-rooms kept at about 40° C. The length of time required necessarily depends on the thickness of the sheets. Thin sheets dry out rapidly in a few days; thicker ones may take quite long periods—up to some months. Evidently, loss of solvent will inevitably lead to shrinkage and distortion of the sheets depending on the amount of solvent present initially.

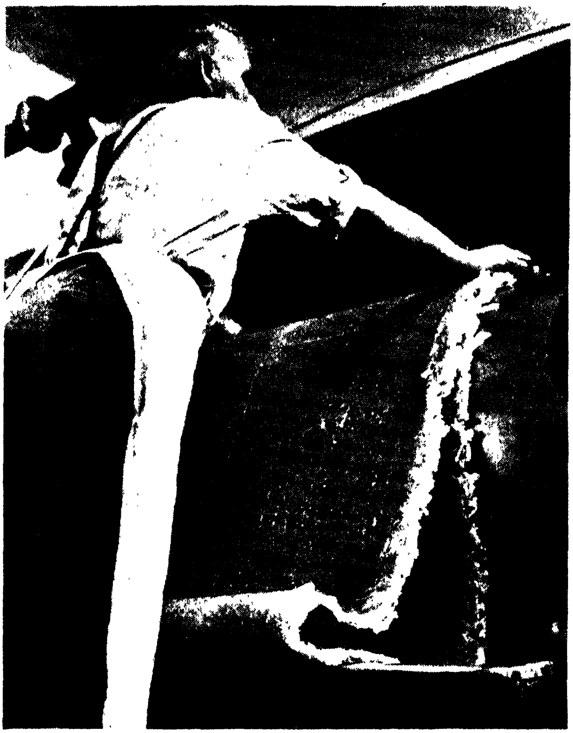


Fig. 125. Mixing cellulose plastics on heated mixing rolls[17]

At this stage there are two defects to be eliminated. There are the knife marks due to the vibratory cutting action; and there is the distortion of the sheets. These are overcome in the final process. The sheets are placed between polished nickel plates and subjected to heat and pressure for a short time. Stacks of these assemblies are placed in multi-platen presses. The plastic sheet flows under the treatment and faithfully reproduces the gloss and polish of the nickel plates. The sheets are cooled before removal. By modifying the surface of the nickel plates any desired surface effect, e.g. matt or polished, will be obtained on the celluloid sheet. Polish on one side and matt on the other is quite a usual type of sheet.

Fig. 126. The slicing machine in action. The knife is fixed, the block of material slides past, and a thin even sheet is sliced off[17]

Extrusion of Celluloid. Tubes and rods of celluloid are made by the process of extrusion. The plastic dough from the mixing mill is fed into the barrel of a standard extruding machine and extruded through a die of suitable shape and size. Alternately, the sheets formed from the dough may be disintegrated into pellets which are fed into the extruder. In either case the tube or rod is extruded continuously and cut to lengths of convenient size. These pieces of celluloid still contain a certain amount of solvent. The presence of solvent accounts for this method being known as wet extrusion. They must be seasoned in order to remove the solvent. During the seasoning process in the warm rooms, rods and tubes shrink and warp to some extent. Consequently they need to be straightened by the process of *trapping*, and they are subsequently polished.

The celluloid is available as standard materials in the form of sheets, rods, and tubes. The dimensions of these forms will vary according to the source of manufacture.

The transparency of celluloid is such that it lends itself admirably to taking colour. It is made in an almost infinite variety of colours and effects. It ranges from water-clear, to pure white at one extreme, to jet black at the other. There is an indescribable range of mottled veined, and grained effects. A full range of colour effects is therefore available, the colours, dyes, or pigments being introduced during the mixing process. According to requirements the colours may be uniform throughout, or a wide variety of effects is obtainable. This is achieved by taking portions of differently uniformly coloured materials and mixing them at a suitable stage of the subsequent handling. For example, in preparing mottled effects two coloured doughs are blended during the rolling or sheeting procedure. The process of blending is one which involves a high degree of skill and experience in order that the effects may be reproduced. There are a number of methods for

Fig. 127. Polishing celluloid and cellulose acetate sheets[17]

producing a whole range of configurations, mottles, grains, etc. The excellent colour values obtained on the basis of clear celluloid is illustrated by the fact that they have been used for making standard colour charts for many years. The shades which are obtainable can be reproduced without difficulty. This is clearly a matter of considerable importance in matching colours.

Properties of Nitro-Cellulose Plastics. The density of nitro-cellulose for making celluloid is about 1·69. The density of a straightforward celluloid composition containing only nitro-cellulose and camphor is about 1·35. The refractive index of clear celluloid it between 1·46 to 1·50. It tends to discolour after long exposure so ultra-violet light or sunlight due to the formation of nitrous gases.

Celluloid is extremely tough, has high tensile strength, and good resistance to abrasion. The top strength obtainable is about 4 tons per sq. inch. It has high impact resistance, and does not splinter when broken. In the ordinary temperature range celluloid is comparatively elastic, becoming plastic at temperatures above 80° C. It shows surprising little tendency for cold flow, retaining dimensions extremely well. This is shown by its use for many years as sheet for production of measuring instruments, etc.

TABLE 79

MECHANICAL PROPERTIES OF NITRO-CELLULOSE PLASTICS

Specific gravity	1·35–1·65
Tensile strength, lb./sq. in.	5,500–8,500
Elongation	Up to 20%
Modulus of elasticity, lb./sq. in. $\times 10^5$	3·5
Impact strength, Izod (notched), ft./lb per in. of notch	Up to 8
Compression strength, lb./sq. in.	25,000
Shrinkage	Up to 1·0%

It is, of course, extremely inflammable. This great disadvantage is reduced by addition of such materials as magnesium, ammonium phosphate.

Celluloid is extremely resistant to moisture. It takes up very little, up to a maximum of 3 per cent, and is one of the best plastic materials in this respect. It is resistant to dilute acids and dilute alkalis. For example, it withstands 30 per cent sulphuric acid almost indefinitely, and for this reason has been extensively used for battery cases. It is, however, attacked both by strong acids and by strong alkalis. Celluloid is very little affected by hydrocarbon solvents, chlorinated hydrocarbons, mineral oils, and vegetable oil. It is affected by solvents such as ketones and esters. Solutions are prepared usually in acetone, ethyl acetate, amyl acetate, etc., and have great industrial importance.

Celluloid is a thermoplastic material and can be moulded under heat and pressure. It can be softened by immersion in hot water above 80° C. It begins to discolour when heated for any length of time at 100° C. For continuous heating the temperature limit is about 60° C. In the normal way temperatures up to 120° C. and pressures up to one ton per sq. inch may be employed for compression moulding. The moulding must be cooled before the article can be removed. Care must be taken about temperature since celluloid becomes troublesome above 110° C. It begins to give off fumes and the characteristic odour becomes apparent. This is very evident in moulding operations.

Fig. 128. Covering metal with cellulose nitrate or cellulose acetate tubing[17]

Celluloid has quite good electrical characteristics. It has not, however, found extended use in the electrical industry owing to its other disadvantages.

Fillers are not usually employed for nitro-cellulose moulding materials or for sheets. Wood flour is used as a filler for nitro-cellulose cements or adhesives. In these it retards shrinkage during drying, so that shrinkage does not cause the film to pull away from the base material.

TABLE 80

ELECTRICAL PROPERTIES

Volume resistivity, ohms/cms. (75% R.H.)	10^{11}–10^{12}
Breakdown voltage, 50 cycles, volts/mil	450–1,000
Dielectric constant, 50 cycles	6·5–9
10^6 cycles	6
Power factor, 50 cycles	0·060–0·15
10^3 cycles	—
10^6 cycles	0·071–0·1

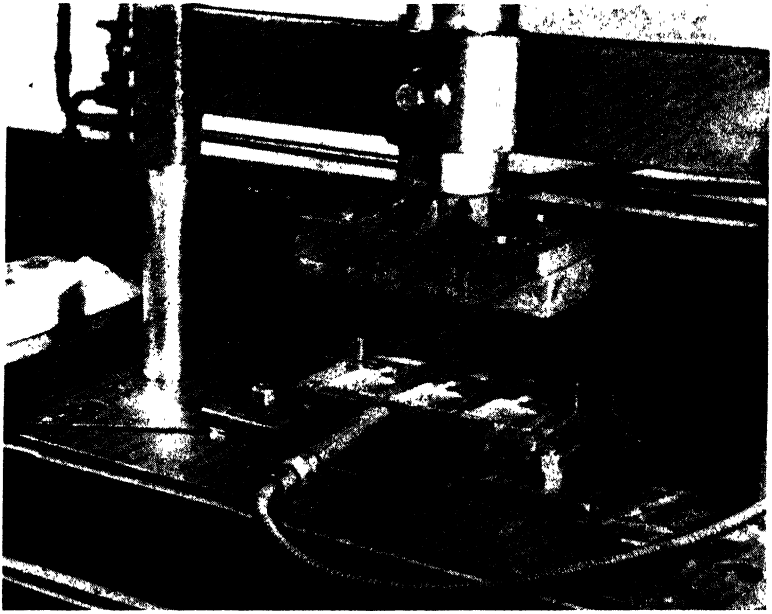


Fig. 129. Blowing celluloid articles showing the mould[17]

Such cements are useful for plugging holes and for filling cracks and crevices, as well as adhesives for securing porous materials, such as earthenware, wood, fibrous composition, etc. These are the compositions sometimes referred to as "plastic wood."

Manipulation of Nitro-Cellulose Plastics. Almost the outstanding characteristic of nitro-cellulose plastic is the ease of manipulation. As a consequence, celluloid is widely employed for the fabrication of numerous articles. By virtue of its toughness it may be subjected to the ordinary machining processes. It can be sawn, cut, bent, drilled, turned, printed, embossed, etc., with great accuracy and ease. Standard woodworking equipment may be employed for carrying out these operations. The chief precaution necessary is that the temperature should be kept down, otherwise there is a danger of igniting the material by frictional heat. In the usual way this is looked after by cooling the tool with a stream of water.

By virtue of its toughness celluloid is extensively used as attractive coatings for numerous familiar articles. For example, the bars and rails in trains, buses, tramcars, etc., are often covered with celluloid. It features as the covering on the handles of sports equipment.

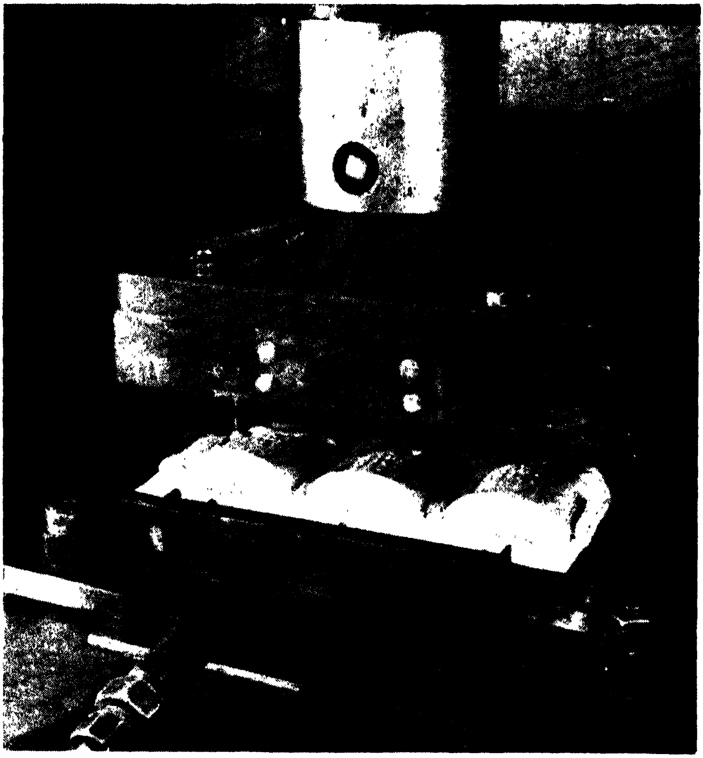


Fig. 130. Blowing celluloid articles showing the finished articles[17]

A very interesting technique is employed for applying the celluloid. It is virtually shrunk on to the article. Celluloid tubing of the requisite dimension is taken and immersed in hot water. It becomes soft and is stretched on a suitable mandrel. It is then chilled, sets, and may be removed. The tube is then drawn over the article to be covered, and is subjected to warming. Heat causes it to shrink tightly on to the base. The method is used for bicycle pumps. Another similar application is for the scuffing on the heels of women's shoes; in this case as a covering for the wooden base.

The usual procedure for applying celluloid to the wooden heel of a shoe is to immerse the celluloid in a solution of 100 parts by weight alcohol, 25 parts acetone, and 25 parts water. This has the effect of softening the celluloid, so that it can be stretched. It is stretched over the wooden former and allowed to evaporate. An adhesive is normally applied to the wood in order firmly to anchor the celluloid. Many other articles are covered in this manner.

Blown Celluloid. Blown celluloid toys and other articles are very widely used, for example floating toys and table-tennis balls are outstanding articles. They are usually made from sheet 0·0015 inch thick. The technique adopted in making these is quite simple. Two thin sheets of celluloid are preheated on hot plates. They are then placed between two heated metal plates having matched cavities corresponding either to a ball or to a floating toy, etc. The plates are subjected to hydraulic pressure. A tiny nozzle is inserted between the sheets through a groove cut into one of the plates. Hot air or steam is then forced in through the nozzle, causing the sheets to conform to the mould surfaces. The whole system is then chilled and the article is removed. The "flash" at the joint is finally trimmed off.

One of the most useful characteristics of celluloid, whether in sheet form or any other form is the ease with which parts can be cemented together or stuck to other materials. Celluloid articles may be cemented together by application of suitable solvents or solutions which may contain acetone, ethyl acetate, amyl acetate, and so on.

For example, one method of making joints is:

First roughen the parts to be joined with sandpaper. A solution of 60 parts acetone and 40 parts amyl acetate is applied to the surfaces, which soften. The parts are then allowed to dry off under pressure.

TABLE 81

SOLVENT ADHESIVES FOR NITRO-CELLULOSE PLASTICS[4]

(*a*)	Dibutyl phthalate	100 parts
	Butyl acetate	50 parts
	Ethyl acetate	50 parts
(*b*)	Tricresyl phosphate	5 parts
	Monoethyl ether of ethylene glycol	100 parts
	Acetone	5 parts
(*c*)	Tricresyl phosphate	25 parts
	Ethyl oxybutyrate	100 parts
	Ethyl alcohol	25 parts
(*d*)	Diethyl phthalate	50 parts
	Dioxan	100 parts
	Ethyl alcohol	50 parts

Application to other materials such as wood, metals, etc., is achieved by the use of suitable cements, which generally contain celluloid. The most usual cements are made up of discarded celluloid photographic film. The procedure is extremely simple and as a consequence fabrication of celluloid presents no difficulties, and accounts for the widespread use of the material.

TABLE 82

TYPICAL COMPOSITIONS OF CELLULOID ADHESIVE SOLUTIONS[4]

Composition by weight, %:	A	B	C
Celluloid, virgin scrap, high viscosity	10·0	25·0	10·0
Acetone	90·0	75·0	45·0
Amyl acetate	—	—	45·0
	100·0	100·0	100·0

One of the most interesting commercial applications of this principle is sticking celluloid to wood.

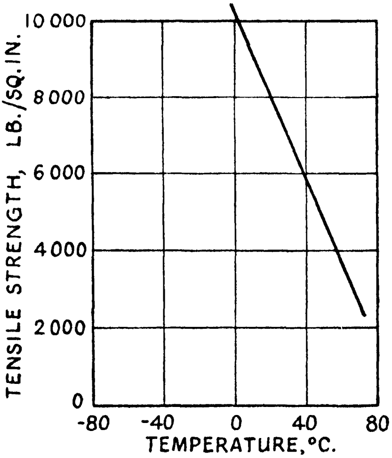


Fig. 131. Tensile strength of cellulose nitrate plastic

Other Applications. Being a highly attractive decorative material, celluloid has been widely used for toilet articles such as brushes, mirror backs, dressing-table sets, etc. It has also found wide application for knife handles, piano keys, fountain pens, propelling pencils, and so on.

By virtue of its exceptional toughness and strength combined with transparency, celluloid has found very wide application. The field has become even wider owing to the fact that celluloid takes print without any difficulty. Ordinary printing technique is applied. Subsequently if the printed surface can be subjected to heat and pressure for a short time, the print is permanently impressed. In this manner it has been used for dials, lenses, watch glasses, mathematical instruments, and so on, for many years. This technique has resulted in its wide application for many fancy articles.

Leather Cloth. One of the most important applications of cellulose nitrate, which occupies a status between that of lacquer and plastic, is in the manufacture of leather cloth. For this application, cellulose nitrate is generally plasticised with castor oil. An extremely flexible film is obtained in this manner which has great strength and maintains its properties over long periods. Solutions are made up on this basis, and these are applied to suitable fabrics by means of rollers, etc. The solution is dried off by passing the impregnated fabric over steam chests, leaving the fabric coated with cellulose nitrate plastic.

A whole range of decorative effects in different colours may be obtained, and special surface effects such as embossed graining or mottling may be applied by calendering or other processes. This process is the basis of such well-known materials as "Rexine," "Pegamoid," etc.

Production of Artificial Leather (Leather Cloth). The production of leather cloth is still of outstanding importance although other materials are now encroaching in the field. Notable ones are ethyl cellulose and polyvinyl chloride. Leather cloth is made on a large scale by treating cotton fabrics with cellulose lacquers or "dopes." The "dopes" generally consist of scrap celluloid, solvents, large amounts of castor oil, and camphor, or other plasticiser.[14] The coatings are built up in layers, the first layer having a large proportion of plasticiser, while the top layers have least plasticiser.

Parkes initiated the manufacture in 1855, waterproofing fabrics with nitro-cellulose, or a mixture of nitro-cellulose and camphor, which he called "Parkesine."

Wilson and Story in 1884 described their method of using combinations of nitro-cellulose, amyl acetate, and castor oil. They were able to produce satisfactory leather cloth, possessing the necessary characteristics of strength and impermeability. Modern productions with minor modifications are based on this work.

Annison, in 1898,[6] described the technique of applying a number of coatings by first using a light, thin coating, followed by heavier coatings.

The principles involved were enunciated by Wood and Stevens, in 1898. They showed that elasticity was conferred by the primer coatings and hardness from the outer coatings. To get the best results the first coatings should be adhesive, the inner coatings soft, with excess of oil, and the final coatings hard, with excess of nitro-cellulose.

Early solutions were based on celluloid, i.e. nitro-cellulose and camphor, which contained adequate plasticiser. Subsequently, additional plasticiser was added. The most favoured type is tri-cresyl phosphate, which decreases the inflammability and gives good ageing.

The materials used are applied by means of a spreading machine, similar to the type used for proofing rubber. The fabric is passed under a knife-edge which allows the requisite amount of dope to be applied. The heated fabric is dried by being passed over a steam-heated table and then through a warm drying chamber.

The Modern Method of Leather Cloth Manufacture.[2] The cloth used to make leather should be a fluffy twill affording anchorage for the "dope." The fabric is brushed to raise the nap to assist this action.

In actual practice the first coatings have low viscosity and can penetrate into the cloth base. To aid penetration and wetting, this first coat is applied with the cloth under tension resting on a rubber roller, so that the knife forces the dope into the fabric. Lower viscosity nitro-cellulose is used for these conditions requiring less solvent. The next coat is much more viscous, aimed at giving a heavy coating. The successive layers are applied in such a manner that they join together. There may be six or eight coatings, the speed of coating depends upon the viscosity of the "dope", the dryness of the cloth and the temperature of the hot-chests over which the coated cloth passes. Subsequent coats are light, to produce a firm, hard finish. Each layer of solution softens and partly dissolves the previous one, so that there is perfect adhesion.

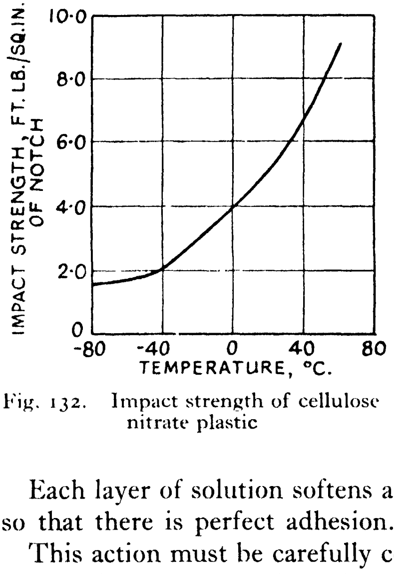


Fig. 132. Impact strength of cellulose nitrate plastic

This action must be carefully controlled so that there should not be too much penetration since this would slow up drying and adversely affect the quality. This is achieved by adding most of the castor oil in the middle layers.

The general principle is to have most castor oil in the inner layers, to give flexibility, and most nitro-cellulose outside to give strength and abrasion resistance. The material is then passed through a heated calender having an embossed roll. The nitro-cellulose softens and acquires the surface and shape of the embossing roller.

Cellulose Foil and Films. One of the outstanding fields of application of cellulose thermoplastics is in the form of transparent sheet material, ranging in texture from the very thin sheets most commonly used for wrapping purposes, up to very thick sheets - almost slabs, used for replacing glass, etc. Technically, the materials are classified according to their thicknesses, as *foil*, *film*, and *sheet*.

Foil is the term applied to material which is made in continuous rolls, and is less than 1/1000th of an inch thick. Foil is familiar as the well-known wrapping materials such as "cellophane." Film applies to the material available in thicknesses ranging up to 15/1000th of an inch.

Yarsley and Couzens divide them into foils and films prepared by a "casting" process, and sheet, which is sliced from solid pressed blocks of the plastic material.

The outstanding use for film in 5/1000 in. thickness is for photographic film base. X-ray film is made in 9/1000 in. thickness. Thicker types are used in the safety-glass industry, and for sturdier wrapping purposes than the foil. Foils and film include those materials which can be prepared from the solution of a plastic by casting the solution and evaporating the solvent.

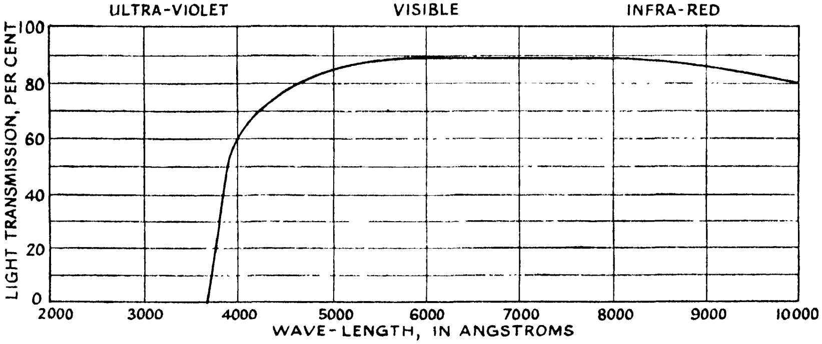


Fig. 133. Light transmission of cellulose nitrate

The best-known foils, films and sheets have been based on cellulose derivatives such as celluloid and cellulose acetate. Of course the most widely used foil, i.e. the "cellophane" type, is based on viscose, which is regenerated cellulose and is really outside the scope of the plastics industry. In recent years, however, numerous other plastics materials have become available in these forms. Among them are ethyl cellulose, polyvinyl chloride, copolymer, polystyrene, pliofilm, etc.

The Background of Transparent Film Materials. The evolution of film has been closely associated with photography. This aspect of the plastics industry and the photographic industry has been actually dependent and contributed to each other's expansion.

Carbutt,[15] in 1884, used thick sheets of celluloid, i.e. nitro-cellulose plasticised with camphor, as the backing for his photographic gelatine emulsion coatings. In 1889 Reichenbach, of the Kodak Company, prepared apparatus for the direct manufacture of roll film support made with celluloid. This was a complete and revolutionary departure from previous practice.

Edison used this film in 1889 for the first ciné film. The invention by Eastman of continuous roll film support was a major industrial development. It clearly owed its success to the availability of a plastic with suitable physical properties; in this case celluloid.

Products of uniform thickness were obtained by the Eastman Company by casting solutions of celluloid on to a rotating drum.

Efforts to use other raw materials in the production of transparent film and foils led to some unexpected developments. When Cross and Bevan[3] had discovered viscose, attempts were made to use this solution to make film. In this case a layer of viscose on a suitable carrier was passed into water and precipitated as a film which contained a great deal of moisture. This could be dried out to a tough, transparent sheet. The outcome of this, after many years' intensive work, was the production of the viscose foils and films such as those known as "cellophane," etc. The natural sequence in due course when cellulose acetate became available was the evolution of cellulose acetate film and foil.

TABLE 83

PROPERTIES OF THIN FILMS

FILMS OF VARIOUS MATERIALS HAVE THE FOLLOWING CHARACTERISTICS

VALUES ON 0·001 INCH FILMS

	Nylon	Ethyl Cellulose	Polyvinyl Formal	Cellulose Acetate	Cellulose Aceto-butyrate
Specific gravity . . .	1·10	1·14	1·23	1·36	1·29
Refractive Index . . .	1·53	1·47	1·50	1·48	1·47
Resistivity—ohms/cm.^{3} .	10^{13}	2×10^{13}	1×10^{13}	$1{\cdot}5 \times 10^{11}$	1×10^{18}
Dielectric strength volts per mil	1,000	1,500	1,000	1,400	1,500
Dielectric Constant 25°C. at 50 cycles . . .	3·2	2·6	3·7	4·3	4·5
Power Factor 25°C. at 50 cycles	0·010	9·003	0.007	—	—
At 1,000 cycles . .	—	0.0025	—	0·0050	0·0048
Water absorption 75 % relative humidity for 24 hours .	5·2 %	2 %	1·3 %	4·9 %	1·0 %

At the present time films are made from these, and also from materials such as cellulose acetobutyrate, ethyl cellulose, polyvinyl butyral, nylon, polystyrene, rubber hydrochloride, etc.

The production of photographic film base is a very difficult manufacture, still confined almost exclusively to nitro-cellulose, while only a very small proportion is made with cellulose acetate. There must be complete freedom from all blemishes. Dimensions must be exact and physical properties quite uniform.

Apart from the photographic and wrapping fields, several other applications of outstanding importance have developed. A notable example is the use of transparent sheets of plastic as the sandwich material in safety glass. The thickness used is of the order of 20 mils–50 mils.

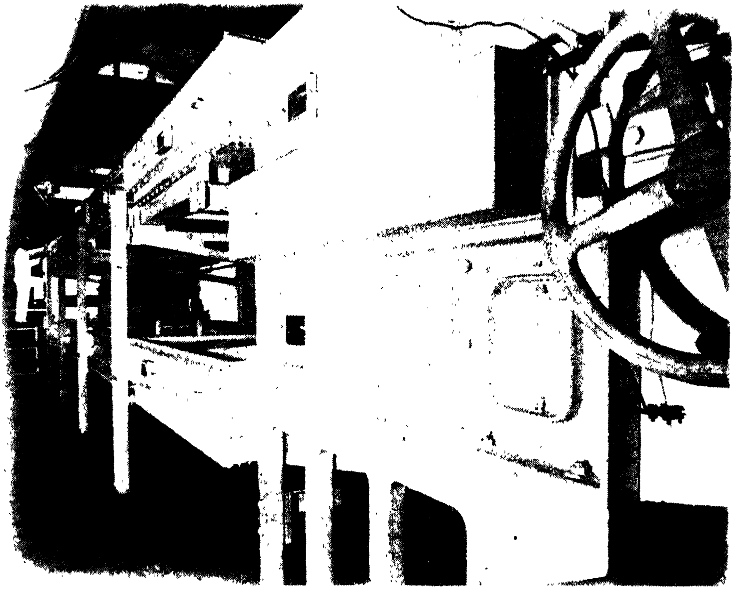


Fig. 134. Film casting machine—continuous band type[17]

The cellulose esters used for film are slightly different from those employed for ordinary plastics. The nitro-cellulose, instead of containing 10·8–11·1 per cent nitrogen, contains 12 per cent, because this is more soluble in ether-alcohol mixture, and it has greater resistance to water. It can be plasticised with a low camphor content, namely, 12 per cent of the weight of nitro-cellulose. Similarly, cellulose acetate used for photographic base contains about 3 per cent more combined acetic acid than that used for ordinary sheeting, mainly on account of increased water resistance. This is an important factor in developing films where there must be long contact with aqueous solutions. Cellulose acetate film is cast from acetone solution. The acetic acid content is as high as possible in order to obtain maximum water resistance. Organic phosphate plasticisers are employed in order to minimise the inflammability as much as possible. The most important use of acetate film is for X-ray photography.

There are two methods[1] for the production of continuous lengths of foil or film:

(*a*) *Continuous band.* Essentially the machine consists of an endless metal band made of copper or nickel, or stainless steel, having a virtually invisible joint. The length may exceed 100 feet, with a usual width of 54 inches. The machine is generally totally enclosed.

(*b*) *Rotating Cylinder.* This is a large cylinder up to 18 feet diameter and 4 feet wide, having a highly polished surface of stainless steel or silver.

Preparation and Application of the Material. For both machines the preparation of material is the same. A solution or dope of the material to be cast is made up, generally a viscous solution with a solid content of about 20 per cent. It is first filtered by passing through a filter press to eliminate any possible foreign particles. The material is then de-aerated, or freed from bubbles. This is achieved by warming the solution, when the viscosity drops and any bubbles may freely move to the surface. It then passes on to the device which feeds it on to the casting band or cylinder.

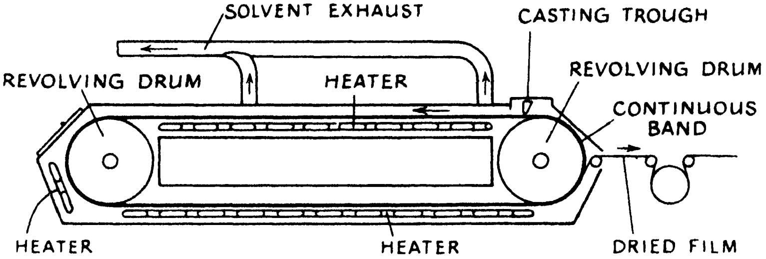


Fig. 135. Diagram of film casting machine

This takes the form of a V-shaped trough, with a slit at the bottom from which the dope may run on to the casting surface. The position of the trough may be adjusted to control the thickness of the deposit. This will also be partly controlled by the speed of the moving band or revolving drum. A normal speed is of the order of three feet per minute, but this will depend on the thickness of the film which is being made.

Continuous Band Method. The film of dope is applied on to the moving band and is carried forward, first through a zone of ordinary temperature, then through successively warmer areas. The whole equipment is usually enclosed in glass. Warming is carried out by the use of steam jackets or coils. In this way solvent is evaporated without the formation of bubbles which would be fatal. The solvent is led away through ducts to suitable recovery plant.

Efficient recovery of solvent is a fundamental essential to successful commercial production, and must exceed 90 per cent efficiency.

By the time the film has made almost a complete rotation of the band it is fairly dry and strong enough to be removed. Final traces of solvent are removed by passing the film through a heated chamber, after which it is coiled.

Continuous metal bands are not yet suitable for direct casting of film. The surface of copper, for example, is not smooth enough. It is therefore covered with a layer of gelatine. By warming this a smooth, glossy surface is obtained. Solutions of cellulose acetate in acetone can be cast on this. On the other hand, solutions of nitrocellulose are troublesome because the solvents used affect the gelatine. This trouble is eliminated by having a film of cellulose acetate cast over the

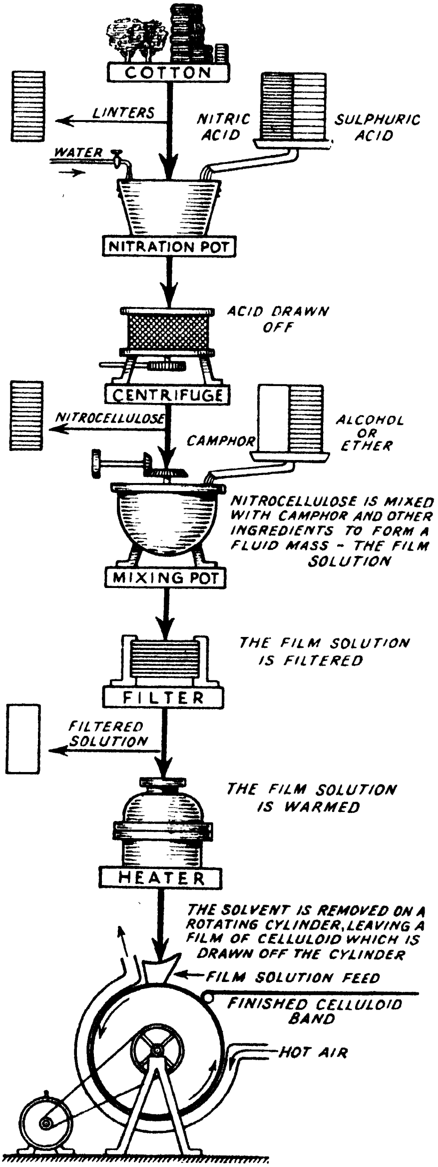


Fig. 136. Production of film

gelatine. Being unaffected by the solvents employed, it acts as the base for the nitro-cellulose solution.

Apart from the method of allowing a heavier coat of dope to form on the band thicker film may be built up by passing the film over another machine and casting another layer over it.

Rotating Cylinder Method. The principles involved are much the same as for the continuous metal band. The cylinder has a steam jacket superimposed which drives solvent off from the cast dope film. After almost a complete turn the film is strong enough to be drawn away, passed through a warm chamber to remove residual solvent, and then coiled.

Production is slower than is possible with the greater length of the continuous band. On the other hand, the ability to polish the surface eliminates the complication of applying gelatine films.

German Photographic Film Base. Photographic film made in Germany were based on the following compositions:

Cellulose Nitrate	
Collodion	100 parts
Ethanol	100 parts
Ether	330 parts
Camphor	11 parts
Butanol	2·5 parts

Cellulose Acetate	
Cellulose acetate (56%)	100 parts
Acetone	320 parts
Ethanol	38 parts
Toluol	19 parts
Dimethyl ether of phthalic acid	5 parts

REFERENCES

1 Bonwitt. "*Das Celluloid*," Berlin, 1933, 445.
2 Clark. *Chem. Met. Eng.*, 1940, **47**, 544.
3 Cross and Bevan. *Berichte*, 1893, **26**, 1090.
4 Halls. *Plastics*, 1941, **5**, 48.
5 Hyatt. U.S.P. 105,338/1870.
6 Jones. "*Cellulose Lacquers*," Griffin, London, 1937, p. 297.
7 Kraemer and Lansing. *J. Phys. Chem.*, 1935, **39**, 153.
8 Lunge. *J.A.C.S.*, 1901, **23**, 527.
9 Parkes. B.P. 2,675/1864.
10 Partridge. *Ind. Eng. Chem.*, 1929, **21**, 1044.
11 Schofield. *British Plastics*, 1942, **14**, 528.
12 Schonbein. *J. Prakt. Chem.*, 1845, **34**, 492; B.P. 11,407/1846.
13 U.S. Figures. United States Tariff Commission.
14 Worden. "*Nitrocellulose Industry*," Van Nostrand, New York, 1911, Chapter II.
15 Yarsley and Couzens. *Plastics*, Pelican Series, London, 1942.
16 Xylonite. Product of B.X. Plastics, Ltd.
17 Photographs by courtesy of B.X. Plastics, Ltd.

CHAPTER XV

CELLULOSE ACETATE AND RELATED PLASTICS

THE outstanding plastic produced from cellulose is unquestionably cellulose acetate. Its importance has grown rapidly in recent years and it has far outstripped other cellulose plastics. There is not the slightest doubt as to its great influence on industry in the future. Although it may not be generally realised, most people come into daily contact with cellulose acetate either as a plastic article, or as film, or as fabric, or as lacquer.

Cellulose acetate is an ester of acetic acid. Up to the present time its production has largely been based on cotton linters, while selected cotton rags have also been used as a source of cellulose. There are indications that it may be possible to produce satisfactory materials from other forms of cellulose. Briefly, cellulose acetate is obtained by treating cotton linters with acetic acid and acetic anhydride in the presence of a catalytic agent such as sulphuric acid.

Evolution of Cellulose Acetate. Credit for the discovery of cellulose acetate is generally attributed to Schützenberger.[13] In 1865, as part of a comprehensive study of cellulose, he examined the action of acetic anhydride and acetic acid on cellulose.

The first commercial materials were made in 1895 by Cross and Bevan, being an offshoot of their comprehensive work on cellulose associated with the discovery of viscose. Their product, however, contained a high proportion of acetyl, i.e. a high proportion of acetic acid had reacted with the cellulose. As a result it was difficult to handle, and had poor solubility dispersing only in solvents which were expensive and toxic. The first plastic type of cellulose acetate was prepared by Eichengrün and Becker[4] in 1903, who introduced the use of sulphuric acid as a catalyst. However, the real turning point in its history came in 1903, when Miles[12] made a number of notable discoveries. He set out partially to hydrolise the acetate by means of dilute sulphuric acid. As a consequence he developed the method for converting insoluble cellulose triacetate into products which were readily soluble in cheap non-toxic solvents. The procedure he developed came to be known as *ripening*.

For some time after this, comparatively little was heard about cellulose acetate until the last war. During the war the production assumed considerable proportions when it was found that solutions of cellulose acetate were able to waterproof and tauten the fabric wings of aircraft.

Satisfactory materials and processes were developed by Henry and Camille Dreyfus. Large-scale activities were sponsored in Great Britain by the Government during the last war. At the end of the war there was a very large production and there was much activity towards finding applications for the material. The outstanding outlet came through the development of methods for making fibres.

The production of yarn from cellulose acetate was pushed with great vigour, and numerous concerns were started. There was a high mortality among these companies. Nevertheless, for a number of years the chief application of cellulose acetate was for the production of yarn.

Another product where cellulose acetate was called for as a replacement of nitro-cellulose was in the production of safety glass for motor-cars. A material was wanted which would not darken and decompose under prolonged exposure to sunlight. The application of cellulose acetate for safety glass was introduced by Cox in 1923.[2] Alongside these advances came the steadily expanding utilisation of cellulose acetate for lacquers and coatings of every description.

Cellulose Acetate as a Moulding Material. The application of cellulose acetate as a plastic for moulding purposes followed only about 1927. After a few years of comparatively slow progress the technique of injection moulding was introduced, which completely revolutionised the trend with regard to cellulose acetate. The application of the intrinsic properties of cellulose acetate to mass production of numerous articles by means of the extraordinarily rapid procedure of injection moulding has led up to the enormous industry of the present day. This industry is still in its early stages.

Some indication of the rate of growth is shown by the following U.S. statistics. In 1929 production of cellulose acetate plastics in the United States was less than two hundred thousand pounds weight. By 1939 it had reached eleven and a half million pounds. This increased to fifteen million pounds in 1940. In the meantime, injection moulding machines had reached a very advanced stage of efficiency. This fact was reflected in the cellulose acetate moulding plastics used in 1941, which reached thirty-one million pounds. By 1943 the output had reached fifty-five million pounds, mounting to sixty-five millions in 1944 and eighty-three million in 1946. It is interesting to compare these figures with nitro-cellulose. This reached a peak output in 1923 of 28 million pounds; in 1937 it was 18 million pounds; in 1940 it was 12 million pounds; in 1941 16½ million pounds; and 18 millions in 1946.

These figures relate only to materials for moulding. The other forms of cellulose acetate plastic, i.e. sheets, rods, and tubes, have also assumed sizable proportions. In 1941 production was 6½ million pounds as against 9 million pounds in the previous year. The explanation of this is that cellulose acetate sheet had lost the bulk of its market for safety glass. The facts are rather interesting. Up to 1934 nitro-cellulose had a virtual monopoly of this field of application. By 1938 nitro-cellulose retained only 20 per cent of the business, while cellulose acetate had the remaining 80 per cent. Yet by 1941 both these two cellulose derivatives shared between them only 1 per cent of the demand! However in 1946 production was almost 20 million pounds.

The Production of Cellulose Acetate. Cellulose acetate is not prepared by treating cellulose in a straightforward manner with acetic acid. The acetylating agent is acetic anhydride. In the action acetic acid is formed as a by-product.

The operations involved in the manufacture are:

(*a*) Pretreatment of cellulose
(*b*) Esterification with acetic anhydride
(*c*) Hydrolysis or ripening
(*d*) Precipitation
(*e*) Washing
(*f*) Drying

Pretreatment involves treatment of the cellulose with small amounts of mineral acids, in order to increase the reactivity of the cellulose, and also to break it down as so to make more soluble products.

Cellulose acetate is produced along the following lines. Cotton linters are dried at a temperature of about 50° C. to a moisture content of less than 4 per cent. Ordinarily the moisture content of cotton linters is 8 per cent. 100 parts of cotton linters are gradually added to a cooled mixture of 200 parts glacial acetic acid, 100 parts acetic anhydride, and 100 parts concentrated sulphuric acid. The mixture is kept below 10° C. The operative material is acetic anhydride.

After about two hours the mixture first becomes fluid and then proceeds to thicken up. During this process the fibrous character of the linters changes, and the progress of the reaction is followed by microscopic examination of this fact. The process is considered to be finished when no cotton fibres remain. Acetylation is carried through to the greatest possible extent, a procedure generally taking something of the order of five hours.

The material formed in this manner is cellulose triacetate, which is soluble only in chloroform, trichlorethylene, etc. It is also known as *primary* acetate. Water is gradually added, carefully, in order that the temperature shall not rise unduly while residual acetic anhydride is being converted into acetic acid.

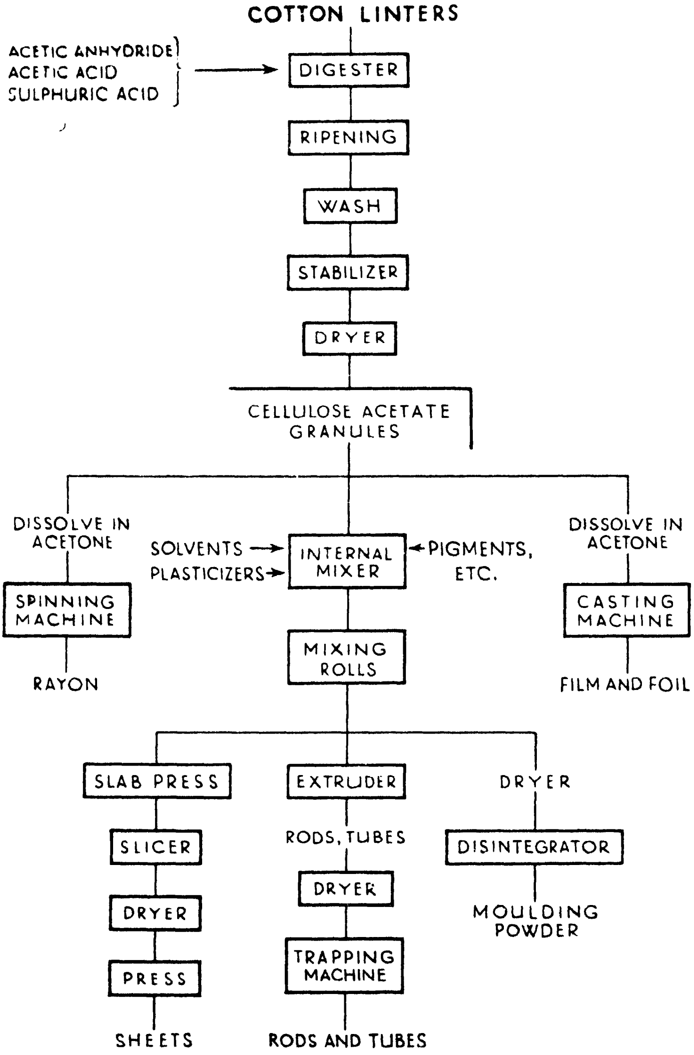


Fig. 137. Flow sheet for cellulose acetate plastics

Since cellulose triacetate is not in great demand it is necessary to treat the material further to produce more soluble forms of cellulose acetate. It therefore undergoes the process of ripening. In this process of ripening acetyl groups split off. In the first place there is a tendency to form cellulose diacetate, and if the conditions are adjusted, this goes even further. Ripening is carried out by allowing the material to stand in large, open copper pans at about 25° C. for four to five days in the presence of dilute acetic acid. During this period acetyl groups are split off and the acetyl value of the cellulose acetate consequently decreases. As this happens, so the material becomes progressively more soluble in acetone. The ripening is allowed to continue until the acetyl value has reached a desired figure. In general practice this is near the value corresponding to cellulose diacetate. As the ripening continues so the material acquires the appearance and texture of golden syrup.

Cellulose triacetate has an acetic acid value (or acetyl value) of 62·5 per cent; cellulose diacetate has an acetic acid value of 48·8 per cent; cellulose mono-acetate has an acetic acid value of 29·4 per cent.

The properties of cellulose acetate such as moisture absorption, solubility, processing behaviour, etc., vary considerably with the degree of acetylation. Therefore the degree to which the primary acetate is ripened is essentially dependent on the specific final application intended.

The final product is obtained from the syrup by careful addition of water, which precipitates cellulose acetate as a finely divided white material. It is centrifuged, washed, filtered, and dried, being obtained finally as a white, flaky mass. This is further well washed with large quantities of water, and is thereafter stabilised by boiling with very dilute mineral acid for about two hours. This has the object of removing any sulphuric esters that may have been formed. The cellulose acetate is then dried at a low temperature, until the moisture content is below 3 per cent. It is then ground to a coarse powder and production batches are blended together.

For use as film for safety glass where specially purified material is desirable the cellulose acetate is further treated by dissolving in acetone, filtering off any particles, and reprecipitating.

The type of cellulose acetate most widely used for plastics has an acetic acid value of 52 to 54 per cent. For applications as lacquer 54 to 55 per cent acetic acid content gives best results.

The amount of acetic acid and acetic anhydride employed in the production of cellulose acetate is very large. Acetic anhydride is an absolutely essential ingredient in making cellulose acetate. It has hitherto been prepared by forming the sodium or calcium acetate, and treating this with sulphur chloride.

Cellulose acetate is primarily dependent on cheap glacial acetic acid. The production of acetic acid in any quantity is assured by the catalytic synthesis from acetylene and new extraction processes from hardwood distillates. Acetic anhydride is also used in large quantities in the production of cellulose acetate (for synthetic fibres as well as plastics) 631,000,000 pounds were produced in the United States in 1948. It is to-day being produced commercially by the interaction of ketene and glacial acetic acid. The development of the commercial production of ketene is a noteworthy step in American chemical industry.

It is essential to attain a very good recovery in order to make the material commercially attractive. The commercial success depends entirely upon the recovery of acetic acid. There are a number of processes which have been developed to attain this object. The final procedure in every case is based on the distillation of dilute acid. In some cases recovery is of the order of 99 per cent of the acetic acid available.

The method used for making cellulose acetate in Germany has been described in some detail.[17]

Method of Manufacture. Cellulose acetate is manufactured using the Hercules methylene chloride process by arrangement with Hercules Powder Co., of America. They produce five standard types of cellulose acetate:

(1) 61 per cent acetyl used for insulation foil production.
(2) 58 per cent acetyl used for non-flam film.
(3) 56 per cent acetyl used for photographic film.
(4) 54·5 per cent acetyl used for textiles.
(5) 52–53 per cent acetyl used for plastics.

The cellulose as received is first dried and passed through a teasing machine to reduce it to a flock. A charge of 1,750 kilos is then loaded into the pretreating machine. The ratio of acetic acid for pretreating was given as 100 parts; 40 parts glacial acetic acid.

The acetic acid is heated to about 60° C. before spraying. The pretreating machine stirrer shaft is started up and then constantly turned while the acetic acid is sprayed through the 24 nozzles during a period of 20 to 30 minutes, and allowed to mix for 2 hours, a temperature of about 50° C. is attained during this process. The charge is then pneumatically transported through ducting to the acetyliser. To the first charge from the pretreater 3,000 kilos of acetic anhydride (95–96 per cent) is added to the acetyliser and mixed for 10–15 minutes, when it is shut down and waits for about 2 hours for the second charge from the pretreater. When this second charge has been added to the acetyliser a further 1,000 kilos of acetic anhydride is added and mixed for 10–15 minutes.

The balance of the acetylising mixture consisting of—

650 kilos acetic anhydride
1,400 kilos methylene chloride
25 kilos sulphuric acid

is added in three equal parts. The first addition is blown in over a period of 30 minutes and temperature is controlled to 15·5° C. by cooling with water at 12° C. When this first addition has been completed the temperature is controlled to 20° C. and the second part of the mixture added over a further period of 30 minutes. The temperature rises to 50° C., and is controlled at this temperature during the third addition, and for a period of 1–3 hours after the last addition, according to acetyl and viscosity requirements. When reaction is complete, temperature is controlled at 40° C. until the required viscosity is obtained. Viscosity tests are carried out in the acetyliser by dropping a 60-gramme weight attached to a long metal rod ¼ in. diameter into the dope and noting the time required for a 20-cm. fall. The weight used is cylindrical, measuring 5 in. long by 1½ in. diameter.

Acetyl content for sampling purposes is determined by precipitating the cellulose acetate by addition of water to the dope sample, the cellulose acetate is dried in warm air and 10 per cent concentration solutions made up. These tests are stated to be as follows:

Solubility in 100 per cent acetone, 58 per cent acetyl.
Solubility in mixture: 5 per cent water, 70 per cent acetone, 25 per cent ethyl alcohol, 56 per cent acetyl.
Solubility in mixture, 10 per cent water: 15 per cent acetone, 75 per cent ethyl alcohol, 54 per cent acetyl.
Solubility in mixture, 22 per cent water: 78 per cent ethyl alcohol, 52 per cent acetyl.

Sodium acetate is used for neutralising the sulphuric acid. When the complete charge has been filtered and passed to the hydrolysing vessel, 2,800 kilos of water are added by spraying over a period of 30 minutes, and then 21 kilos of sulphuric acid in 50 kilos of acetic acid are added and hydrolysis carried out to the required stage. Steam is blown in and a temperature varying between 55° and 80°C. is attained. By this means the methylene chloride is expelled and passes through condensers to a collecting vessel for re-use, last traces of methylene chloride are removed under vacuum (580 mm.).

The cellulose acetate is then precipitated by addition of 8 to 12 per cent strength acetic acid to the hydrolysing vessel. By this method the precipitating cellulose acetate is brought down in fairly large lumps, and in order to break these up, the solution is pumped through an enclosed breaker mill and circulated back to the hydrolyser until a fairly uniform product is obtained, when, by means of valve control, the flow is diverted to a grinding mill, first passing over a wire mesh conveyor, which separates the acid solution and carries the cellulose acetate to the grinding mill.

After grinding the cellulose acetate is transported pneumatically through ducting to a continuous band-washing machine, and from there again through ducting, to a continuous centrifuge, and then to storage silos.

From the storage silos the semi-dry cellulose acetate is blown into the steam-heated vacuum driers and after drying to 2–3 per cent moisture content is passed through further ducts to storage silos, from where it is packed into drums or sacks ready for dispatch.

Cellulose Acetobutyrate. The Hercules patented process is essentially the same as for cellulose acetate, using mixed anhydrides in this case, obtained by distilling together acetic anhydride and butyric acid to give a product of 92–94 per cent mixed anhydrides and 8–6 per cent butyric acid.

The formula was given as:

100 kilos cellulose
350 kilos mixed anhydrides
400 kilos methylene chloride
1 kilo sulphuric acid

Sodium acetate is used for neutralising sulphuric and hydrolysis is effected with 5 per cent sulphuric acid. The final product consists of 17–19 per cent butyral and 42–44 per cent acetyl.

The product was mainly used for insulation films.

Cellulose Tripropionate. Comparatively small amounts of this product were made in Germany (about 3–5 tons per month). The method was stated to be comparable with cellulose acetate manufacture, using propionic anhydride instead of acetic anhydride and sodium propionate for neutralising instead of sodium acetate.

The formula given was as follows:

100 kilos cellulose
400 kilos propionic anhydride
400 kilos methylene chloride
1 kilo sulphuric acid

The product is used for lacquers and insulation film.

The Properties of Cellulose Acetate. A number of different types of cellulose acetate may be obtained according to the acetyl value, i.e. the amount of acetic acid which has reacted with the cellulose. The difference in the behaviour of the various types depends upon two factors, (*a*) the degree of acetylation, that is to say the percentage of acetic acid present, and (*b*) the viscosity of the cellulose acetate in solution. The viscosity is very largely dependent on the mechanical treatment and the temperature to which the cellulose acetate has been subjected during its production.

By varying these two factors an extremely wide range of materials are commercially available having characteristics specifically suited to the application where the cellulose acetate is to be used for plastics, for lacquers, films, rayon, etc.

The outstanding characteristics of cellulose acetate are its great toughness and impact strength. It is very resistant to ultra-violet light which it also transmits extremely well.

It is unaffected by weak acids, oils, greases and most solvents. In particular it resists petrol. Cellulose acetate does not withstand alkalis. Although it burns, in this respect it is incomparably superior to nitro-cellulose. The softening point of cellulose acetate varies, according to the type, between the temperatures of 240° to 300° C. Heated to these temperatures it softens forming a melted mass which thereafter begins to char. This range is too high for ordinary manipulation, and consequently plasticisers must be added to lower the softening temperature. It takes up a certain amount of water, the quantity decreasing as the acetyl content becomes greater. This characteristic, too, is improved by addition of suitable plasticisers. Its permeability to water varies in a similar manner. Cellulose acetate does not break down in sunlight except on very prolonged exposure. Any decomposition products are colourless and transparent sheets remain clear.

Cellulose acetate is not used alone owing to the comparative lack of flow until high temperatures are reached and the tendency to char at these temperatures. It can be dissolved in suitable solvents and excellent products are obtained from such solutions, for example, as films, fibres, and so on. In order to bring out the best properties it is essential to add plasticisers. A variety of effects may be obtained according to the nature of the plasticiser, for example, they improve flexibility, give toughness, and improve moisture resistance, etc.

Behaviour of Cellulose Acetate in Solvents. Cellulose acetate does not possess the wide solubility characteristics of other cellulose derivatives. Cellulose acetate is soluble in a number of different solvents, according to the proportion of acetyl present. These solutions play a very important role in industry. While the present discussion is not directly concerned with cellulose acetate lacquers, yet the preparation of films and sheets depends on such solutions, and solvents play an important role in the preparation of doughs for plastics.

In solution the critical property is the viscosity. One well known convenient method for determining viscosity of cellulose acetate solution —the falling ball method—as used by the Hercules Powder Co.[5] is carried out as follows:

The time of drop of a $\frac{5}{16}$-inch steel ball, through 10 inches in a tube of 1 inch diameter, the solution being 20 per cent cellulose acetate in a mixture of 9 parts by weight acetone and one part alcohol, at 25°C. The result is given as the number of seconds.

The following table summarises the solvent behaviour:

TABLE 84

SOLVENTS FOR CELLULOSE ACETATE

Solvents	Boiling Range °C.
Ethyl formate	54
Methyl acetate	56– 62
Ethyl acetate	85
Acetone	56– 67
Methyl ethyl ketone	80– 85
Dioxan	101
Methyl cellosolve	115–125
Methyl cellosolve acetate	138-154
Carbitol acetate	211–220
Ethyl lactate	119–176
Diacetone alcohol	153–160
Ethylene dichloride-alcohol, 9 : 1	—
Methylene dichloride-alcohol, 9 : 1	—

The outstanding properties of cellulose acetate are, of course, of great value for coatings generally, but in addition cellulose acetate films have other advantages. Cellulose acetate tautens fabric very effectively, a fact which accounts for its extensive use as an aeroplane dope. Suitably compounded films have good dielectric characteristics which accounts for the leading part the material plays in cable lacquers. In this application, too, its resistance to petrol and oil enhance its value.

Cellulose acetate foil is extensively used as transparent sheeting for wrapping purposes. Its film has low moisture absorption compared with viscose cellulose film, so that it does not tend to wrinkle on a package. As a consequence it has found wide application for packing purposes. It is unaffected by various foods and fruits normally packed in transparent wrappings. It can be sealed rapidly by moistening with a suitable solvent. Having high strength and being extremely flexible thin sheets of transparent cellulose acetate can be fabricated or moulded into more rigid types of containers, which have a wide appeal. It is also extensively utilised as a foil for electrical insulation.

Properties of Cellulose Acetate Film. Cellulose acetate film is also the chief basis employed for safety film, which is now so widely employed since it has not the fire hazard of nitro-cellulose film. Up to the present time it has not been possible to acquire the same characteristics with cellulose acetate film as with celluloid film, particularly in such properties as flexibility, etc. Until this becomes possible celluloid film will continue to hold the main market.

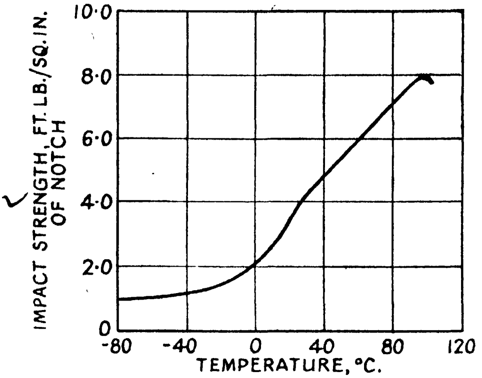


Fig. 138.
Impact strength of cellulose acetate

Windows are cut from such sheets. Lenses are stamped from thick sheet stock. Cellulose acetate sheeting containing a fluorescent dyestuff which can be illuminated by ultra-violet light is extensively used for indirect lighting.

Heavier forms of cellulose acetate film are used for numerous industrial and agricultural purposes; for example, it is employed for making cloches for agricultural use; it is used to replace glass in greenhouses, and the like, because of the ability to transmit ultra-violet light. Heavy sheets are used for a variety of display and decorative purposes. They are also employed reinforced with wire for skylights and protective windows generally.

The Preparation of Cellulose Acetate Film. A solution of cellulose acetate in acetone is made up containing some plasticiser. The dope contains 25 per cent acetate plus about 40 per cent of plasticisers such as dimethyl phthalate or diethyl phthalate. It is clarified by passing through a filter under pressure in an enclosed filtration plant. It is allowed to stand for a time until free from bubbles. The film is prepared by casting on to a moving band. The casting machine consists of an endless band running over rollers. It is totally enclosed in glass. At one end over the top of one of the rollers is the casting device. In effect this is a V-shaped trough with a slit at the bottom, located immediately above the band. It is arranged so that the level of the top is kept constant by an automatic feed from a main supply of filtered material. The copper band has a thin coating of gelatine. As it moves past the slit a thin layer of dope passes on to the band and is carried forward. It passes through zones of gradual increase in temperature which drives off the volatile acetone. This passes through exhaust outlets which carries the solvent-laden air to a recovery unit. At the other end of the band the cast film, which by this time is substantially dry, is stripped off. It may be further dried by passing through a hot area, and is then wound on to a mandrel. In this manner cast film of unlimited length can be obtained. The thickness of such films may vary from 1/1000th of an inch upwards. By passing films on to successive machines thick films may be obtained. The wide bands, possibly several feet wide produced in this manner, may then be slit mechanically to any desired width.

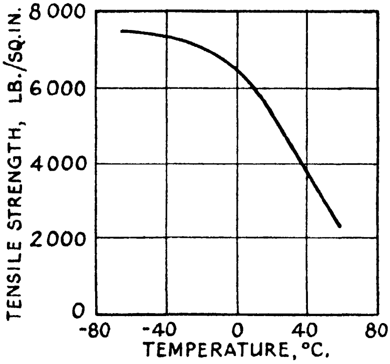


Fig. 139.
Tensile strength of cellulose acetate

Table 85

Properties of Cellulose Acetate, Film and Sheet

	Film (Unplasticised)	Sheet	Coloured Sheet
Specific gravity	1·36	1·25–1·36	1·25–1·50
Refractive Index n_D	1·48	1·47–1·50	—
Ultra-violet light, transmission	92%	91%	—
Tensile strength, lb./in.^{2}	5,000	3,000–8,000	2,500–9,000
Elongation, %	7–10	20–50	20–50
Wet tensile strength, lb./in.^{2}	4,000	2,000–6,000	—
Wet elongation	10–15	—	—
Modulus of elasticity, lb./in.^{2}	$2{\cdot}2 \times 10^5$	$1{\cdot}5 \times 10^5$	$2{\cdot}5 \times 10^5$
Sward hardness (glass 100)	78	60–78	—
Softening point	250° C.	50–240° C.	70–110° C.
Surface resistivity, ohm./cm.^{2}	$1{\cdot}5 \times 10^{10}$	10^{10}–10^{12}	—
Dielectric strength, v. mil.	1,400	600–1,000	300–800
Dielectric constant, 1,000 cycles	6	4·5	10
Power factor, 1,000 cycles	0·005	0·08	0·12
Water absorption, % weight, immersion 48 hours	6	2–4	1·5–4

Cellulose Acetate and its Plasticisers. As a plastic, cellulose acetate is virtually useless alone. Plasticisers have had a profound influence on the development of cellulose acetate for plastics. No single material has yet been found which is able to influence cellulose acetate in the same way as camphor plasticises cellulose nitrate. Almost every known possible material has been tried and by a process of elimination a number have been found to behave fairly satisfactorily with cellulose acetate. In general, however, it is necessary to use a blend of plasticisers to give the desirable characteristics.

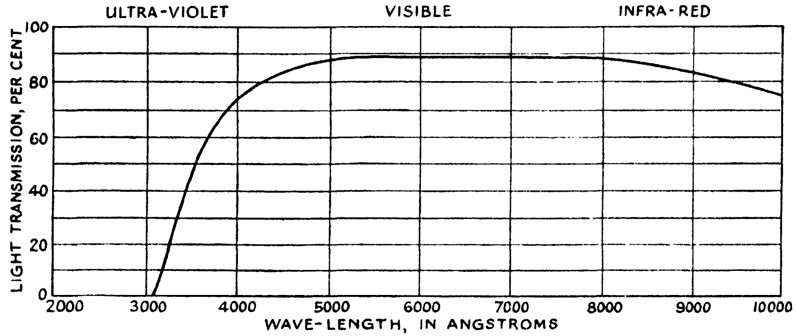


Fig. 140. Light transmission of cellulose acetate

The functions demanded of any plasticiser in cellulose acetate are:

(*a*) To enable the material to be converted into a uniform plastic mass.

(*b*) To lower the melting point to a convenient workable temperature.

(*c*) To improve properties such as water resistance, toughness, hardness, flexibility, resistance to dimensional changes, flame resistance, light resistance, resistance to the effect of oils, fats and greases.

The following list outlines some of the leading materials used in cellulose acetate compounding:

TABLE 86

PLASTICISERS FOR CELLULOSE ACETATE

Plasticisers	*Effect*
Camphor	Produces surface hardness and retards evaporation of other plasticisers; makes material brittle: discolours
Dibutyl tartrate	Solvent; toughens; water-sensitive

TABLE 86—*continued*

Plasticisers	*Effect*
Diethyl phthalate	Softener; water-resisting; cheap; non-solvent; volatile
Trichlorethyl phosphate	Gives non-inflammability with flexibility
Dimethyl phthalate	Water-resisting; solvent; volatile
Ethyl p-toluene sulphonamide	Solvent; toughens; discolours, shrinks
Ethyl phthallyl ethyl glycollate	Toughens; softens
Methyl phthallyl ethyl glycollate	Toughens; solvent; volatile
Methyl cellosolve phthalate	Solvent; toughens; tendency to sweat
Triacetin	Solvent; toughens; water-soluble; volatile
Tributyl phosphate	Solvent; toughens; non-inflammable, volatile
Triphenyl phosphate	Hardener; flame-proofing; sweats; non-solvent
Acetates of Mannitol, Sorbitol, and Sucrose	Hardeners; non-volatile; embrittling if used in excessive amounts
Diphenyl phthalate	Hardener; non-volatile

Compounding Cellulose Acetate. In formulating plastic compositions based on cellulose acetate a number of considerations must be taken into account.

Cellulose acetate depends for its use largely on the ease of manipulation, particularly by injection moulding; it also depends on its attractive appearance; clearly the physical properties are also fundamental.

In the first place it is necessary to find out the influence of the nature and quantity of plasticiser on such factors as toughness, hardness, cold flow, softening point, cold crack, temperature, and so on. In addition, depending on the application of the material, the effect on colour, odour, taste, electrical characteristics, handling characteristics, and so on, must also be borne in mind.

Then there are the considerations involved in the manipulation of the material as a plastic; that is to say, the influence of these plasticisers on the moulding characteristics. For example, injection moulding calls for different types of acetate according to the article being made. The ease with which the material will become fluid, its rate of flow under pressure, the way in which it cools, its shrinkage, and so on, are all characteristics of the greatest practical importance. For example, it is a difficult problem to achieve the necessary softness at moulding temperature, and yet have correct rigidity and toughness at ordinary temperatures.

Certain definite points emerge from such considerations of plasticisers. The density of the cellulose acetate plastic will depend on the amount of plasticiser present. So far as strength is concerned useful materials usually contain between 60 to 75 per cent of cellulose acetate. Fluid plasticisers in general exert a marked softening action, lowering tensile strength and hardness. Other characteristics such as elongation, impact resistance, and cold flow tend to increase. Solid plasticisers such as triphenyl phosphate exert a hardening action whereby elongation and cold flow are lowered, but the impact resistance and toughness are correspondingly also lowered.

The Preparation of Cellulose Acetate Plastics. The conversion of cellulose acetate into plastic masses is carried out in an internal mixer usually jacketed and hooded. Cellulose acetate is mixed with the requisite plasticisers and with volatile solvents. A typical mix is as follows:

Cellulose acetate (acetyl value 52%)	100 parts
Plasticiser	35–40 parts
Solvent	100 parts

The plasticiser is usually a blend such as equal parts of dimethyl phthalate and diethyl phthalate. The solvent is usually a blend of equal proportions of acetone, alcohol, and benzene.

The acetone acts as a solvent for the cellulose acetate in the cold, while hot alcohol and benzene also act as a solvent for acetate. This mix would apply for clear transparent products. Soluble dyestuffs give coloured transparent material, while pigments give opaque and coloured products.

The mass is then mixed in steam-jacketed internal mixers, which generally have vacuum equipment. Mixing is carried out at 30° C. to 40° C., being continued until a homogeneous mass is obtained. The mixing generally takes about 3 hours. A pale yellow dough-like mass is formed. Much of the solvent mixture is carried off during the mixing and passes on to a solvent recovery apparatus.

The dough-like mass is passed through a filter press under pressure of something like 3 tons per sq. inch, when all dirt and foreign matter is removed. It is then rolled on mixing mills so that a thick blanket of material is formed round the front roller. The mill is warmed, and more solvent passes off into the hood which surrounds the machine. The material thickens up during this rolling procedure owing to loss of solvent. It is then taken off the rollers as a slab about an inch thick. Thereafter the treatment to which it is submitted will depend upon the application of the final material.

Production of Sheets. For the production of coloured or transparent sheets of material the following process is generally applied. The thick slab from the mill is cut into suitable pieces which are placed into a large steel block mould in a press. There is a loose metal base plate to the mould. The block is subjected to pressure at 400 lb. per sq. inch at 90°C. for 6 hours. It is then cooled under pressure for some hours. Upon removal from the press a large block of cellulose acetate plastic is obtained, attached to the metal base plate. This is mounted on a slicing machine and sheets are then mechanically cut in thicknesses ranging from five-thousandths of an inch upwards.

At this stage the sheets still contain about 10 per cent of solvent which must be removed. This removal of solvent is known as the *seasoning* process. The sheets are hung in hot air for periods which may vary from two days for thin sheets up to several months for thick sheets. But in this way the sheets shrink about 10 per cent of the dimensions. The surface of the sheets are marked with the striations made during the cutting process. These have to be removed. The sheets are placed between two highly polished nickel plates. Six or more sets of such plates are assembled in each aperture of a press. Multi-daylight presses are used for this work which may take as many as 20 stacks of plates. The sheets are pressed at 95°C. for several minutes, and are then cooled off. They come out with an absolute reproduction of the high polish of the plates. By the use of plates with suitable surfaces matt finish or any other desired effects may be obtained.

In this manner decorative highly coloured polished sheets may be obtained which have very wide application. An unlimited range of effects, mottles, and so on are made available by mixing suitable coloured compositions prior to the slabbing procedure. These sheets have the advantage that by comparison with celluloid they are virtually non-inflammable; they burn quite slowly. They have outstanding merit for aircraft use. They are resistant to petrol, naphtha, toluene, etc. They are non-corrosive, impervious to water and non-shattering.

Large quantities of transparent sheets of every thickness are made in this manner. They have many uses for safety glass, aircraft windows, cockpit covers, and so on. They are widely used for drawing instruments, for dials and lenses, for cloches and so on.

Cellulose Acetate for Low Temperature Insulation. A most interesting application of cellulose acetate sheet is in the form known as Isoflex.[11] made by B.X. Plastics, Ltd. This consists of corrugated sheets of cellulose acetate stuck together in alternate directions so as to give a composite structure. This is a system of air spaces made from a material of low heat conductivity. The resulting material is an excellent low temperature insulator, which is extremely light. The following table illustrates how it compares with other materials:

TABLE 87

HEAT INSULATING PROPERTIES OF SOME MATERIALS[11]

	Thermal conductivity C.G.S. units	Thermal conductivity B.T. units	lb. per cubic foot
Isoflex	·00011	·32	0·75 lb.
Slab cork	·00009	·25	6·0 lb.
Granulated cork	·00010	·28	6·5 lb.
Cork wool	·00007	·21	3·3 lb.
Expanded rubber	·00010	·28	4·0 lb.
Expanded ebonite	·00007	·22	5·4 lb.
Wood wool	·00010	·28	—
Glass fibre	·00010	·28	—
Diatomaceous earth	·0002	·56	30·0 lb.
Wood fibre board	·00013	·38	—
Slag wool	·00010	·29	15·0 lb.

It is already widely used for refrigeration purposes, for insulating railway vans, marine refrigeration, etc., and has possibilities in house construction.

Extrusion Methods. After the rolling treatment on the mixing mill as already described, cellulose acetate may be sheeted out thinly, and then provides the stock for extrusion. This still contains solvent. The preparation of rods and tubes is one of the largest outlets for cellulose acetate. In this case they are extruded and put aside to season before carrying on to the final process of straightening and polishing. However, extrusion may be carried out with the moulding powders prepared from this stock, that is, after all solvent has been removed.

Extrusion compounds based on cellulose acetate are now made by dry mixing methods. This is possible because much higher proportions of plasticisers are employed. Cellulose acetate, plasticisers, pigments, etc., are premixed and then subjected to milling on mixing rolls at high temperature or in hot internal mixers. The plastic mass formed in this way is extruded.

One outstanding development in the extrusion field is the production of extruded sections to serve as edgings for tables, counters, furniture, and profiles for chairs.

Preparation of Moulding Powders. The moulding powders are prepared as follows: In the procedure for making sheets, thick slabs are taken from the mixing mill. For moulding powders thin sheets of the cellulose acetate plastic are taken off the mixing rolls and set aside to dry off. The dried sheets are then passed through rotary crushers which reduce them to small particles. These constitute the moulding powder which is being used on an increasingly large scale all over the world.

Cellulose acetate plastics may be moulded by two standard methods,

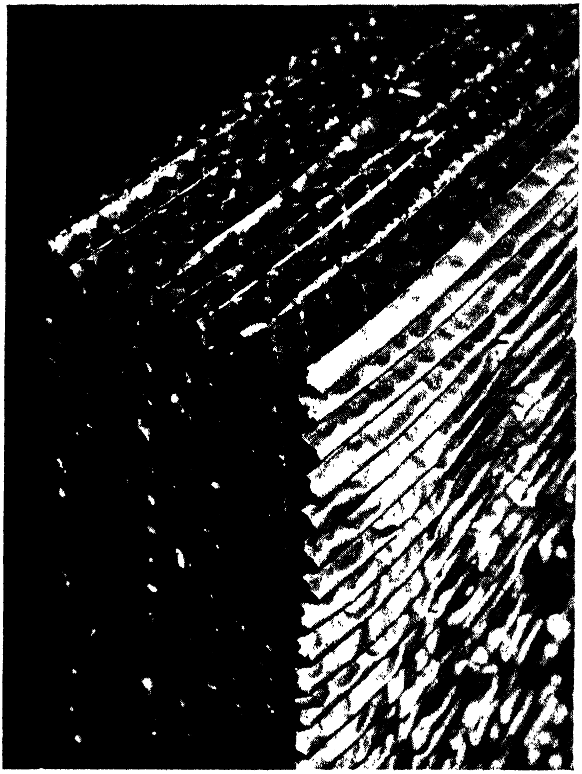


Fig. 141. Isoflex-thermal insulator material based on cellulose acetate[16]

—compression moulding and injection moulding. Compression moulding is carried out along the lines used for thermoplastic materials generally, that is to say, the moulding powder is placed in a mould between the platens of the press. More usually blanks are stamped out of suitable cellulose acetate sheet. The press is closed, the cellulose acetate flows under heat and pressure and takes up the shape of the mould. Since the moulded article is thermoplastic when hot, it cannot be removed in this condition, consequently the mould must be chilled before the article can be removed. It is quite clear that this must be a

Table 88

General Characteristics of Cellulose Acetate Mouldings[8]

Group	Colour	Ash %	Nature of Pigment and Mineral Filler	Specific Gravity at 20°C.	Water Absorption (24 hrs. at 20°C.) %	Loss on Heating (6 hrs. at 110°C.) %	Softening Point, °C.	Remarks
Cellulose acetate	Clear colourless	0·2	Nil	1·32	1·8	2·2	83	No loading
Cellulose acetate	Brown	4·5	Dyestuff, manganese and iron oxides	1·34	2·3	2·3	84	Inorganic fillers as well as dyestuff or lake
Cellulose acetate	White	15·0	Aluminium and zinc oxides	1·44	1·7	2·1	87	
Cellulose acetate	Yellow	18·5	Aluminium lake colour, siliceous earth and aluminium oxide	1·45	3·0	2·8	87	
Cellulose acetate	Black	1·0	Aluminium lake dyestuff	1·32	2·9	3·1	86	No loading
Cellulose acetate	Brown	2·5	Aluminium lake and iron oxide	1·34	4·8	2·6	95	15% wood flour filler
Cellulose acetate	Black	0·44	Dyestuff	1·31	1·2	1·1	83	Note: Coloration without appreciable inorganic material
Cellulose acetate	Grey	0·46	Dyestuff	1·33	0·8	1·1	84	
Cellulose acetate	White	0·86	Dyestuff	1·31	2·2	1·0	87	
Cellulose acetate	Green	0·51	Dyestuff	1·33	2·3	1·0	85	
Cellulose acetate	Red	0·87	Dyestuff	1·34	2·8	1·0	87	
Cellulose acetate	Maroon	1·15	Dyestuff	1·27	3·2	0·6	87	

relatively slow process, especially for large articles. While cellulose acetate could only be moulded in this slow manner it could not make any spectacular headway.

The introduction of injection moulding has completely altered this outlook. It was essential for the economic development of cellulose acetate. It introduces economy of moulds, time, labour and scrap—while giving enormous output facilities. Its application arises from the fact that cellulose acetate is relatively stable while hot, and can be maintained hot and fluid in a chamber for quite long periods. In this condition it can be injected into a cold mould where it cools very rapidly, becoming sufficiently rigid to hold its shape, and can be ejected almost immediately. Metallic inserts may be used with the injection moulding process.

Fillers are not used to any great extent with cellulose acetate. For some special purposes wood flour is sometimes used to prevent shrinkage of mouldings during cooling. Fillers adversely affect most of the characteristics particularly the toughness and flexibility.

Properties of Cellulose Acetate Moulding Powders. The outstanding characteristics which account for the widespread use of cellulose acetate moulding powders may be summarised as :

1. Wide range of attractive colours, including transparent and translucent.
2. Ease of injection.
3. Free flow and rapid setting.
4. Good tensile strength and toughness.
5. Uniformity.
6. Good insulating properties.
7. Resistance to oils, weak acids and weak alkalis.
8. Good polish and low heat conductivity, giving a surface pleasant to the touch.
9. Low flammability.
10. Low specific gravity.

Articles made from cellulose acetate by injection moulding have many attractive properties which account for the extraordinary expansion in the use of the material by injection moulding. Because mineral fillers are not very extensively used, the specific gravity of mouldings are quite low.

Cellulose acetate moulding powders flow readily presenting few difficulties in injection moulding, and set very rapidly when chilled. The temperatures used range from 145°–260° C., while injection pressures range from 4 to 15 tons per sq. inch. Compression moulding

TABLE 89

CHARACTERISTICS OF SOME TYPICAL CELLULOSE ACETATE MOULDING POWDERS[8]

Colour	Clear Colourless	Brown	White	Yellow	Black	Brown
Analysis, per cent:						
Cellulose acetate, dry basis . .	97·3	91·5	82·7	78·0	95·0	78·5
Wood flour, dry basis . .	Nil	Nil	Nil	Nil	Nil	15·0
Moisture	2·7	4·0	2·8	4·5	4·5	4·5
Mineral pigment or filler . .	—	4·5	14·5	17·5	0·5	2·0
	100·0	100·0	100·0	100·0	100·0	100·0
Nature of Colorant	Nil	Spirit soluble dye	Mineral	Aluminium lake	Aluminium lake	Aluminium lake and mineral pigment
Nature of mineral pigment or filler .	Nil	Oxides of iron and manganese	Oxides of aluminium and zinc	Aluminium oxide	Nil	Iron oxide
Particle size, per cent:						
Retained on 20 mesh . .	20	85	86	80	85	90
Passing 20, retained on 40 mesh .	40	10	12	15	12	7
Passing 40, retained on 60 mesh .	36	3	2	5	2	3
Passing 60 mesh	4	2	0	0	1	0

is carried out at temperatures from 130°–150° C. with pressure from $\frac{3}{4}$-ton to 2 tons per sq. inch. The shrinkage obtained in the mould ranges from 0·002 inches per inch up to 0·01 according to the composition.

TABLE 90

MOULDING PROPERTIES OF CELLULOSE ACETATE

Compression moulding temperature	130–150° C.
Compression moulding pressure, lb./sq. in.	1,000–2,400
Injection moulding temperature	145–250° C.
Injection moulding pressure, lb./sq. in.	10,000–30,000
Tendency to cold flow	Slight
Mould shrinkage (cold mould to cold piece):	
Injection	·002–·003 inches/inch
Compression	·005 inches/inch
Resistance to heat, ° C. (continuous)	60–80° C.
Distortion under heat, ° C.	50–95° C.

Uniform products are obtained in the widest possible range of attractive colours, either transparent, translucent or opaque.

TABLE 91

MECHANICAL PROPERTIES OF CELLULOSE ACETATE

Specific gravity	1·28–1·40
Refractive Index, n_D	1·47–1·5
Compressive strength, lb./sq. in.	12,000–20,000
Tensile strength, lb./sq. in.	3,000–9,000
Elongation	10–50%
Flexural strength, lb./sq. in.	6,000–9,000
Impact strength (Izod)	2–5 ft. lb. per in. of notch
Modulus of elasticity, lb. per sq. in. × 10^5	1·5–4·2
Brinell hardness (10 kg. load)	6–7·5

They are very little affected by sunlight. So far as ageing is concerned, they change but slightly over very long periods, the change being associated with slow losses of plasticisers according to their volatility. The refractive index of transparent colourless material is from 1·47 to 1·50.

The mouldings take an excellent polish from injection moulds. They have low heat conductivity and are pleasant to handle.

Almost the outstanding feature of cellulose acetate mouldings is their great toughness. This is supported by high impact strength, tensile strength and other mechanical characteristics.

Physical Properties. Naturally, softening temperatures will depend on composition. Softer types may begin to flow at 50° C.

while very hard types may not flow until 100° C. They will stand up to continuous temperatures of between 60°–80° C. according to their composition.

They have no odour or taste. While they are unaffected by water, they tend to take up a certain amount which for some applications may be excessive and is a disadvantage. This property is profoundly influenced by plasticisers which are generally chosen to reduce moisture absorption. Thus after 24 hours immersion the water absorption may range from 1·5 per cent up to 7 per cent.

They are only slightly affected by weak alkalis and weak acids. On the other hand they are decomposed by strong alkalis and strong acids.

Cellulose acetate mouldings are usually soluble in acetone, in ethyl acetate and other acetates, in lactates, in acetone, in tetrachlorethane, in mixtures of ethylene dichloride and alcohol, in essential oils, and so on. They soften in alcohol, and higher esters, and tend to swell in chlorinated hydrocarbons. They are insoluble in ether, in benzene and other aromatic hydrocarbons; they are insoluble in aliphatic hydrocarbons including petrol. Nor are they affected by animal oils, vegetable oils, mineral oils, greases, etc.

They have good electrical insulation behaviour although this is adversely affected by the somewhat high water absorption.

TABLE 92

ELECTRICAL PROPERTIES OF MOULDED CELLULOSE ACETATE

Volume resistivity, ohms/cms. (50% R.H.)	10^{12}–10^{13}
Breakdown voltage, 50 cycles, volts/mil. (instantaneous)	300–850
Dielectric constant, 50 cycles	4·5–6·0
10^6 cycles	4·4–4·7
Power factor, 50 cycles	0·01–0·04
10^6 cycles	0·04–0·10

One of the most important features which commends them from the commercial point of view is that there is very little scrap associated with manufacture. All rejects, buffings, etc. are thermoplastic and if clean may be disintegrated to granules and used again.

Cellulose Triacetate. In recent years cellulose acetate of much higher acetyl content has come into favour. Materials with acetyl content up to 58 per cent have been made. These have been described by Gloor.[7] The outstanding features are the considerably enhanced resistance to moisture and the better resistance to heat. Apart from these characteristics plastics based on these materials behave in much the same way as ordinary cellulose acetate. Because of the improved moisture resistance, products have better gloss, lower shrinkage, and better resistance to weather. It is important also that these plastics can be mixed with standard cellulose acetate plastics, for example, in the injection moulding machine.

Cellulose Acetobutyrate. In recent years mixed esters of cellulose have appeared, and some have gained wide commercial application. Actually these were first made by Cross and Bevan,[3] but the commercial materials are based on the much later work of Clark and Malm[1] in 1932. Outstanding examples are cellulose acetopropionate, and cellulose acetobutyrate. It was discovered that these mixed esters had rather superior properties when compared with straightforward cellulose acetate. In particular, water absorption was notably better. They are soluble in a wider range of solvents, miscible with more plasticisers, resins, etc. Plasticisation does not present such difficulties as with cellulose acetate. Moreover the flow characteristics of these materials were also markedly superior to those of cellulose acetate compositions.

As a consequence they have come into large scale production and usage in the United States. Outstanding in this respect are the cellulose acetobutyrate moulding powders which appeared in 1938 as *Hercose C* made by Hercules Powder Co.,[9] and *Tenite* 2 made by Tennessee-Eastman.[14] It is found that with these materials, the same degree of plasticity can be obtained with the use of far less plasticiser than for cellulose acetate. Fordyce and Meyer[6] have illustrated this aspect extremely well.

The production of cellulose acetobutyrate introduces the necessity for large amounts of butyric acid. At the present time the shortage of this material makes production in this country rather difficult. However, it seems that such form of production would be desirable in the future. The usage in the United States already runs into very large quantities.

Cellulose acetobutyrate has the desirable mechanical properties possessed by cellulose acetate, being just as tough and strong. It is far better where cellulose acetate is at a disadvantage notably in its high water absorption. Thus it takes up less than half as much water as cellulose acetate on prolonged immersion. It has superior temperature resistance and has better low temperature behaviour.

The Hercules materials contain a minor proportion of butyric acid, all types containing between 18–22 per cent butyric acid, and 42–38 per cent acetic acid. One of the best solvents for the material is ethylene dichloride, a 12 per cent solution being convenient for most purposes.

The work of Fordyce and Meyer was based on rather different proportions. They suggested that cellulose acetobutyrate with 35–40 per cent butyric acid should be used. Much of their work was with a material composed of 37 per cent butyric acid and 13 per cent acetic acid.

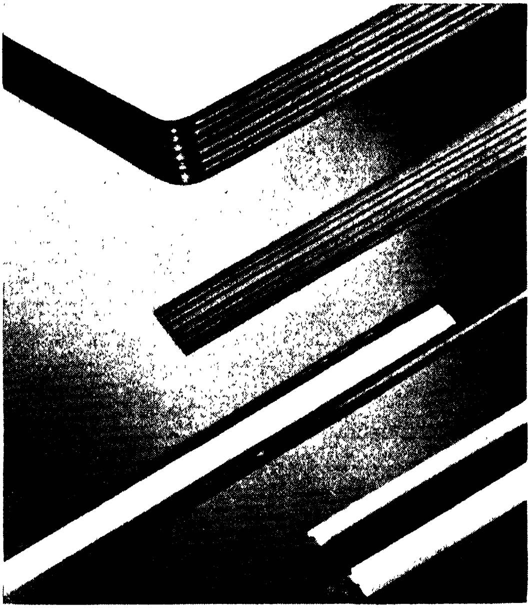


Fig. 142. Edgings and beadings extruded in cellulose acetate

They showed that to produce equivalent flow characteristics in cellulose acetobutyrate required far smaller quantities of plasticiser than in the case of cellulose acetate.

The I.G. Plant at Dormagen in 1944 was producing the following cellulose acetate derivatives:

	Tons per Month	Application
Cellulose Acetate, 54–55%	220	Silk
56–58%	80	Safety film
52·5–53%	80	Plastics and lacquers
Cellulose Triacetate, 61–61·5%	10	Insulating foil
Cellulose Acetobutyrate, 40% acetyl 20% butyryl	10	Lacquers and foils

TABLE 93

COMPARISON OF PHYSICAL PROPERTIES OF PLASTIC COMPOSED OF CELLULOSE ACETATE (38·5 PER CENT ACETYL) AND CELLULOSE ACETOBUTYRATE (37 PER CENT BUTYRYL, 13 PER CENT ACETYL) WITH VARIOUS PLASTICISERS.[6]

	Dimethyl Phthalate					
	Cellulose Acetate			Cellulose Acetobutyrate		
Parts plasticiser, 100 parts base	37·8	30·0	22·6	15·8	11·0	6·3
Flow temp. °F.	266	285	307	266	285	307
% elongation	8·0	6·5	5·0	23·8	22·7	21·8
Tensile strength, lb./sq. in.	6,630	8,100	9,930	4,690	5,520	6,540
Flexural strength, lb./sq. in.	11,140	14,200	17,000	7,840	9,240	10,950
Rockwell Hardness, M.	79·5	90·5	101·1	72·4	80·1	86·4
% Water absorption (48 hr.)	2·13	2·47	3·24	1·45	1·58	1·68
% leaching (48 hr.)	0·58	0·52	0·45	0·41	0·29	0·22
% loss in wt. (1 wk. at 150°C.)	2·40	0·86	0·53	1·60	0·60	0·46
% shrinkage (1 wk. at 150°F.	1·38	0·11	0·09	0·89	0·48	0·19
	Diethyl Phthalate					
Parts plasticiser, 100 parts base	59·5	49·0	38·7	17·0	12·0	7·0
Flow temp. °F.	266	285	307	266	285	307
% elongation	40·0	28·6	20·8	26·2	24·7	23·4
Tensile strength, lb./sq. in.	2 860	3,850	5,100	4,410	5,340	6,470
Flexural strength, lb./sq. in.	3,930	6,050	8,800	7,390	8,920	10,800
Rockwell hardness, M.	49·0	59·7	75·5	65·5	75·2	84·3
% water absorption (48hr.)	1·78	2 13	2·38	1·40	1·48	1·82
% leaching (48 hr.)	2·18	1·11	0·52	0·33	0·27	0·20
% loss in wt. (1 wk. at 150°C.)	6·67	3·85	1·96	0·54	0·40	0·21
% shrinkage (1 wk. at 150°F.)	3·02	1·53	0·70	0·33	0·27	0·13
	Dimethoxyethyl Phthalate					
Parts plasticiser, 100 parts base	62·5	51·3	39·6	18·5	13·2	7·8
Flow temp. °F.	266	285	307	266	285	307
% elongation	49·2	33·3	25·0	28·9	26·7	24·6
Tensile strength, lb./sq. in.	2,760	3,700	4,880	3,710	4,680	5,870
Flexural strength, lb./sq. in.	3,670	5,700	8.390	6,430	8,240	10,480
Rockwell hardness, M.	20·6	44·3	67·2	60·1	71·2	82·0
% water absorption (48hr.)	2·64	2·90	3·23	1·58	1·73	1·79
% leaching (48 hr.)	1·98	1·62	0·51	0·26	0·20	0·15
% loss in wt. (1 wk. at 150°C.)	0·41	0·34	0·23	0·19	0·17	0·13
% shrinkage (1 wk. at 150°F.)	0·29	0·21	0·17	0·13	0·11	0·09

REFERENCES

1 CLARK AND MALM. *J.A.C.S.*, 1929, **51**, 274; B.P. 313,408/1929; U.S.P. 2,038,005/1936.
2 COX. U.S.P., 143,094/1923.
3 CROSS AND BEVAN. *Researches on Cellulose*, Longman's, 1908, p. 90. Series II.
4 EICHENGRÜN AND BECKER. B.P. 21,628/1903.
5 Falling Ball Method. Technical literature of Hercules Powder Co.
6 FORDYCE AND MEYER. *Ind. Eng. Chem.*, 1940, **32**, 1053.
7 GLOOR AND GILBERT. *Mod. Plastics*, 1940, April 17th, p. 62; *Ind. Eng. Chem.*, 1941, **33**, 597.
8 HALLS. *Plastics*, 1942, **6**, 267.
9 Hercose C. Product of Hercules Powder Co.
10 Hercules Powder Co. U.S.P. 2,292,516/1942.
11 Isoflex. *British Plastics*, 1941, **13**, 3.
12 MILES. U.S.P. 733,729; 828,350/1903.
13 SCHÜTZENBERGER. *Comptes Rendues*, 1865, **61**, 485.
14 Tenite 2. Product of Tennessee-Eastman Corp.
15 U.S. Cellulose Acetate. United States Tariff Commission.
16 Photograph by courtesy of B.X. Plastics, Ltd.
17 C.I.O.S. XXXIII-23, p. 112.

CHAPTER XVI

THE INJECTION MOULDING PROCESS

VAST numbers of articles are being made by the process of injection moulding. The size of these articles has been growing rapidly as the size of injection moulding machines grows. Articles such as golf tees, thimbles, combs, spectacle frames, bobbins, coil formers, are now being joined by very substantial car parts, aircraft parts, refrigerater accessories and so on.

Injection moulding is the process which consists of feeding a granulated thermoplastic material into a heated cylinder through which it is forced progressively forward by a plunger which may be driven by hydraulic, mechanical or pneumatic means. The amount of material allowed into the cylinder is automatically controlled. The thermoplastic softens under the heat and becomes virtually fluid. The hot fluid material finally passes through a nozzle or orifice or *gate* into a tightly locked mould. This mould is made up of two parts. It is kept at a low temperature to assist the hot plastic to cool and become rigid. The set article may then be ejected without losing its shape. In the case of small products a large number can be made at a single shot. The mould is designed to have the requisite number of apertures all of which are connected by channels which lead into the main feeding gate. Many machines are operated automatically or semi-automatically. A few small hand-operated units are used chiefly for experimental purposes.

Materials which are nowadays universally fabricated by injection moulding include cellulose acetate; cellulose acetobutyrate; polystyrene; methyl methacrylate resins, etc. The main characteristics involved are those of ready flow under heat and pressure, and heat stability.

Implications of High Temperature. The use of high temperatures clearly has several important implications for the material. Material for injection moulding must not contain volatile solvents or volatile plasticisers. Moreover, the powders must be free from moisture, otherwise bubbles will be formed which may spoil the product. Precautions are particularly necessary for transparent products from materials such as methacrylate moulding powders, or polystyrene, where desirable optical effects are completely spoiled by bubbles.

It is quite general practice nowadays to preheat moulding powders in order to remove any moisture. The powders are warmed to about 80° C. in trays before being moulded.

The heat resistance of plastics should not be confused with the heat resistance of particular colours. The former has to do with the stability of the plastic base and plasticisers, the latter with the stability of the colouring agents used in producing any particular shade.

The necessity to heat and cool the mould during the compression process was a deterrent from the use of cellulose acetate as a moulding plastic. Injection moulding supplied an ideal alternative inasmuch as only applied heat was necessary.

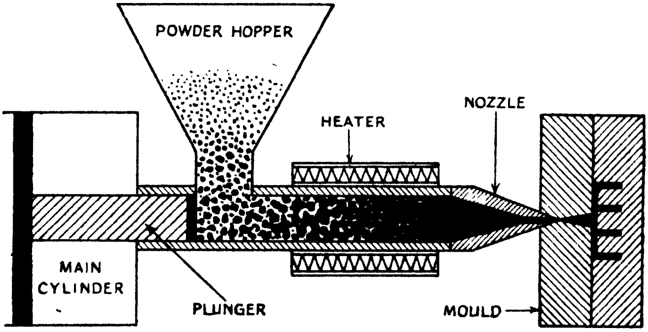


Fig. 143. Principles of injection moulding[8]

Injection moulding implies heating a plastic material in a cylinder to a plastic condition, then forcing it by means of a plunger through an orifice into a cold (or relatively cool) mould. The cavities are connected with the nozzle of the heating cylinder by channels through which the plastic material flows.

The Process is Extremely Rapid. The outstanding advantage of injection moulding is the rapid rate of production. The process has far outstripped in speed and capacity the limits reached by compression moulding of any material. The advantages are accompanied by the fact that a large number of cavities can be filled simultaneously. There are limitations of design. Articles which have undercuts, etc., cannot be injection moulded. The reason is that they cannot be ejected, and this factor offsets any other advantages.

Some indication of the possibilities of injection moulding can be obtained from the fact that at the present time there are machines which can mould articles weighing 36 oz., four times every minute. Mouldings 3 ft. by 4 ft. in dimensions have been made by injection at this rate. Even such articles as bath tubs are visualised as being feasible by this method.

Injection moulding increases the scope of plastics. Awkward deep drawn shapes which cannot be made by press moulding are possible by injection. It becomes possible to produce mouldings of difficult shapes and intricacy due to the fact that the plastic is squirted into the closed mould. It enables the moulding of thin walled articles with flanges. Mouldings can be made with small metal inserts.

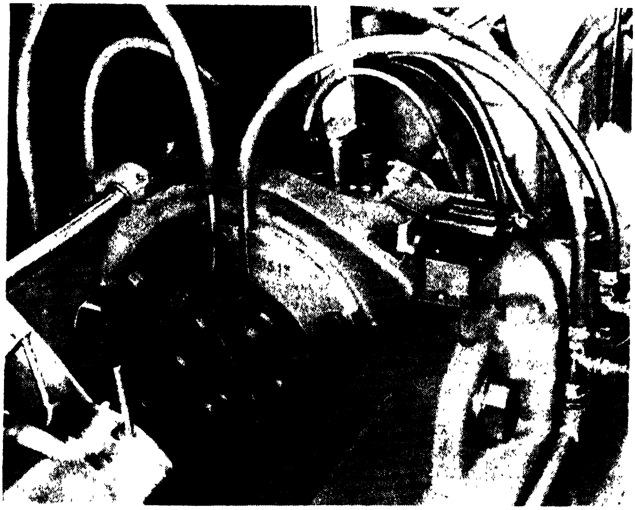


Fig. 144. Open mould of an injection moulding machine[8]

Metal cores can be covered by injection moulding. Moreover, it is quite unnecessary for the core to be more than the general shape of the finished covered piece. No expensive finishing of the insert is necessary. Covering a metal core combines the toughness and beauty of the plastic with the rigidity of the metal.

An outstanding product of this type which is extensively produced by injection moulding is the covering of steering wheels, usually carried out with cellulose acetate.

The injection moulding machine was very necessary for the economic and technical development of cellulose acetate plastic. Having attained this object for cellulose acetate, the same possibilities have been applied to many other thermoplastics, including ethyl cellulose, other cellulose esters, polyvinyl copolymer, acrylic plastics, methacrylate plastics, polystyrene, etc.

Background of the Process. The original conception of such a machine was borrowed from metal practice. It is attributed to Pelouze,[6] who in 1856 invented a die-casting machine for forcing molten metal into a die by mechanical or hydraulic pressure. Oddly enough the first application of this machine to plastics was made by Hyatt[4] in 1872, who used a somewhat similar machine for extruding celluloid. The machine he used had many features which are found on present-day injection moulding machines. Cellulose nitrate was not a very suitable material for handling by this method, and consequently the possibilities at that time were discounted. This is an outstanding example of a technique waiting for a suitable material. It could only come into service when a plastic arrived, which was thermoplastic, stable and fluid, at high temperature. The arrival of stable cellulose acetate moulding powders met the requirements.[2] It has been followed by numerous other plastics, such as polystyrene, ethyl cellulose, acrylic plastics, etc.

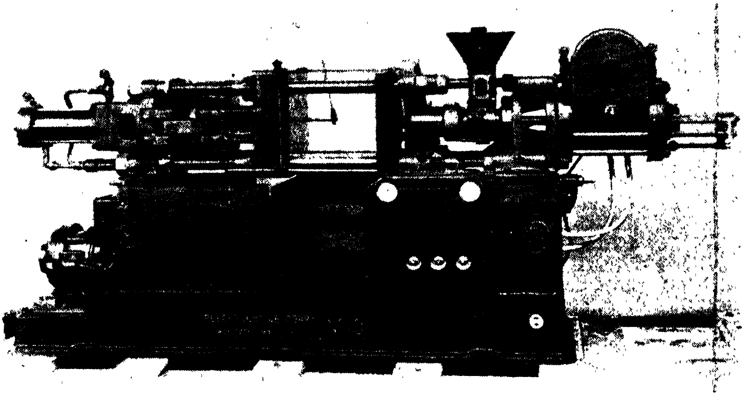


Fig. 145. Reed-Prentice injection moulding machine—open[9]

Following great activity in Germany, Buchholz,[1] in 1931, patented a procedure for injection moulding of thermoplastic materials. At this time machines were operated by hand. Gastrow,[3] in 1936, described the heating cylinder used on the Isoma machine which two years before was the first injection moulding machine to be made commercially available. The early machines were capable of injecting up to $1\frac{1}{2}$ oz. per cycle and could be used only for making small articles such as buttons, combs, and jewellery. The machines were relatively crude and inefficient in the early days, tending to obscure their real promise. The comparative slowness showed no great advantage over straightforward compression moulding.

Technicians in the United States were quick to see the possibilities of such machines and much work was put in on this problem. This was greatly stimulated by the mounting demands of moulders. American activities led to radical changes in the design of heating cylinders, spreading devices, injection plungers and clamping devices. As a consequence half a dozen United States firms have vied with each other in turning out bigger and better machines year by year. The capacity of the machines has grown by leaps and bounds. More and more automatic features were introduced, cutting down labour costs to a minimum. The acme would appear to have been reached in the modern completely automatically operated machines. The development of these machines has been extremely rapid. It may be gauged by consideration of the increasing capacity of single cylinder injection machines. By 1936 the best capacity had risen from 2 oz. to 4 oz. per cycle; in 1937 it was 6 oz.; it reached 9 oz. in 1938, and 12 oz. in 1939. In 1942, it was 22 oz. The maximum area of the moulded part possible in 1937 was 40 sq. inches; by 1939 it had reached 100 sq. inches. The trend at the present time is towards the use of multiple cylinders which feed through different inlets into the same mould. In this way a charge of 36 ozs. may be injected.

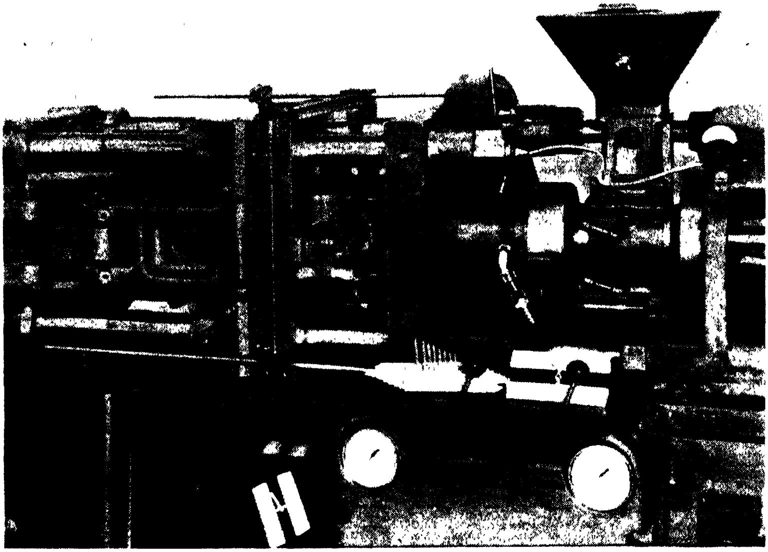


Fig. 146. Reed-Prentice injection moulding machine—closed[9]

Macht, Rahm, and Payne[5] have summarised the three clearly defined, well-designed types of injection moulding machines as follows:

> "*Completely Hydraulic.* Hydraulic power is used for the closing and locking of dies, as well as for the forcing of the plastic through the material cylinder.
>
> "*Mechanical.* All operations are mechanically carried out. Power is supplied from a crank for locking moulds and forcing the plunger forward. Follow-up pressure is maintained by springs.
>
> "*Combination Hydraulic and Mechanical.* Hydraulic power is used to force the material through the stock cylinder, and the dies are locked by a mechanical toggle or wedge, which in general is actuated by a second hydraulic cylinder.
>
> "It is estimated that there are approximately a thousand of these three types of injection machines in commercial use in the United States. While each specific type has its proponents, they all give eminent service."

Advantages of Injection Moulding. Injection moulding has many advantages which have revolutionised the position of thermoplastics:

(*a*) A high speed of production is possible. There is no necessity for alternately heating and chilling, as in compression moulding of thermoplastics. There is no need for curing.

(*b*) A low mould cost is made possible by the smaller number of cavities required per mould for a given production.

(*c*) The dies are of lighter construction than those used in compression moulding.

(*d*) Flash is not formed in a well-made injection mould. The products require less finishing. The stalks formed in the channels or "runners" are broken off, or clipped.

(*e*) There is no waste of material. All defective articles and the material in the channels connecting cylinder and mould are thermoplastic, and can be used again. They are ground and remoulded alone or mixed with new stock.

(*f*) The method shows a high thermal efficiency, for the heating cylinder and chilled moulds are maintained at constant temperatures throughout the cycle.

Some Operating Features. Even with machines of the largest capacity, very short cycles are possible, e.g. up to 12 cycles a minute. It is not general practice to work machines of high capacity very rapidly for articles with large cross section. The poor thermal conductivity of plastics which cause difficulties in heating uniformly, likewise operates to slow the chilling of the article in the die. The time of the cycle is decided primarily by the thickness of the article. So that while thin articles may be moulded at very high rates, e.g. a cycle of a few seconds, yet thick articles may require several minutes.

In present-day machines the plunger which applies the pressure is automatically controlled. The mould is automatically closed and opened by another control. The moulding powder is fed into the heating chamber by a measuring device actuated by the plunger. Injection of the moulded article is also an automatic procedure. The injection cylinder is usually heated by the thermostatically controlled electric coils by induction or by means of hot oil, etc. The size and design of the orifice nozzle is generally varied according to the size of the article being moulded.

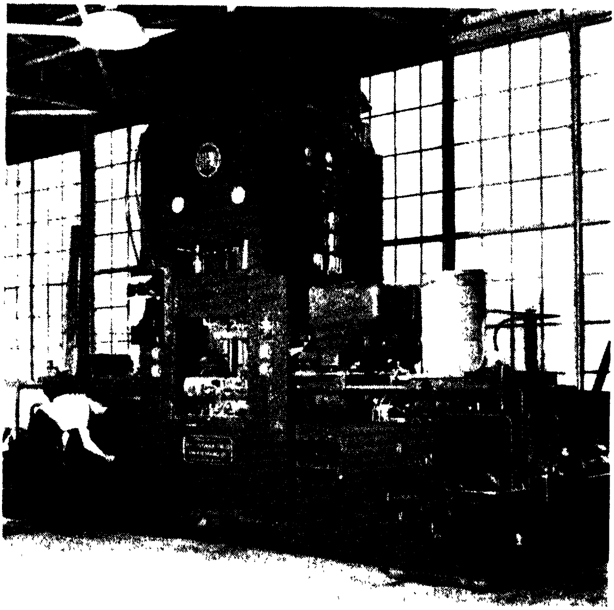


Fig. 147. H.P.M. injection moulding machine with multiple inlets

The essential feature in injection moulding is to force the plastic into the mould at a sufficient speed that the mould is completely filled before the material sets by contact with the cold metal. If this rapid filling of the mould is not attained, then:

(*a*) The article will lack high finish.

(*b*) Strains and stresses will be set up and there will tend to be laminations.

Thus high speed and high pressures are essential. They also are necessary to produce a polished surface on the moulded article. Premature setting of the surface leads to the setting up of undesirable strain which may tend to give unsatisfactory surface to the final product. Cold material is fed in one end and heated fluid plastic is ejected from the other end. The plasticising capacity, and hence the weight and number of shots per hour is the amount of plastic which can be raised to the requisite temperature while it is in the cylinder.

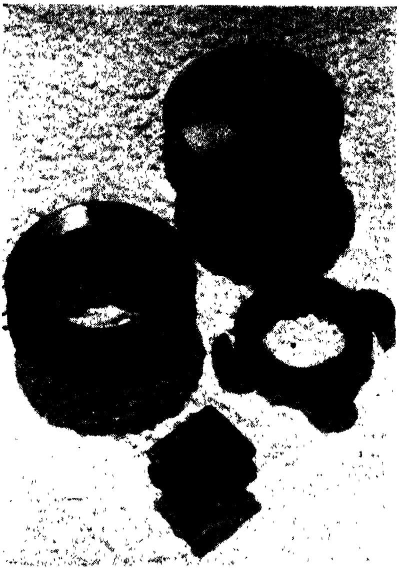


Fig. 148. Typical articles moulded by injection moulding[8]

It is essential to use comparatively high temperatures in injection moulding. These are higher than the temperatures used for compression moulding. This is necessary because the material tends to cool off during its passage into the mould. In the earlier stages of development this high temperature introduced many difficulties. It was almost impossible to attain uniform heating of the mass of material being forced through the cylinder. Means for overcoming this were developed. In modern machines an obstruction, a spreader, is provided —torpedo-shaped, or pineapple-shaped, etc. The plastic material flows around this and between it and the cylinder as a thin layer. This layer can thus acquire a more uniform temperature. A die is fixed in front of the heating cylinder. This leads the hot plastic through the gate and runners of the mould.

Another feature is that the temperature of the heating medium is much higher than the temperature of the material, and the material must not be left in the cylinder longer than is absolutely necessary, otherwise there may be overheating and scorching. The temperature of the plastic when the mould is filled must in general be higher than the temperature used for compression moulding. Generally material left stationary in the cylinder will char or decompose; so that when the machine is stopped for any reason, heat is turned off, and the usual practice is to continue pushing the material through until the temperature has dropped sufficiently.

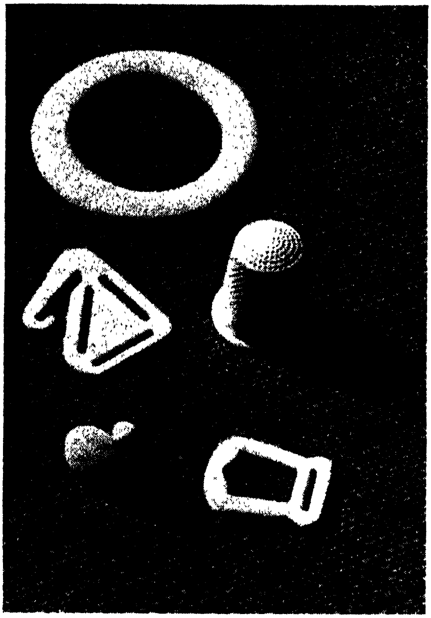


Fig. 149. Articles made by injection moulding[8]

Temperatures of the injection cylinder may be between 175° and 200°C. The actual temperature used will depend on a number of factors such as the composition of the plastic, its flowing characteristics, and the type of moulding being made. The same factors will decide what injection pressure will be employed, possibly ranging between 6 to 20 tons per sq. inch, depending on the material, etc.

Design of the gate (or entrance orifice of the mould) and runners is of great importance. If too small and long they obstruct the flow of material. If they are too large they take longer to set and pressure must be maintained on the mouldings, while the set sprues and runners must be clipped away. *Sprue* is the solid plastic filling the tapered gate. Mould design has been admirably considered by Smith.[7]

The Action in Injection Moulding. Consider the flow of plastic into the mould. The ram forces the plastic through the nozzle into the gate, in the form of a continuous wave. Passing through the gate, the plastic enters the runners and flows into the cavity through a restricted opening. Frictional heat, due to the travel through the runners and cavity entrance, helps to maintain the plastic in a softened condition. Obstructions in the mould, such as inserts and pins, will divide the wave and chill it slightly.

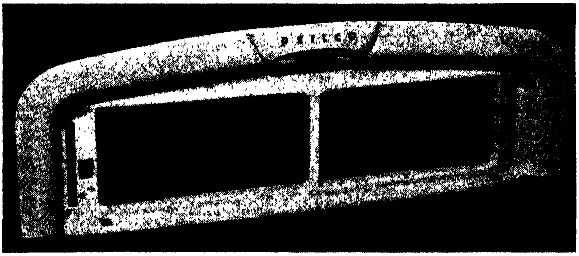


Fig. 150. Example of a large article made by injection moulding

The divided wave will meet again, after surrounding the obstruction, to fill completely the cavity. Air in the cavity is forced ahead of the plastic wave and must escape by means of knockout pins, sleeves or suitably placed vents. If the air is not allowed to escape, it becomes compressed, sets up pressure, and causes local burning of the stock due to heat of compression. Also there is an incompletely filled cavity.

With the cavity filled, the ram maintains pressure sufficiently long to cause the sprue to set before withdrawing. The mould is kept closed long enough to allow the moulded pieces to set sufficiently to be ejected without distortion.

Moulds. The moulds employed for injection moulding are very costly, especially when multiple mouldings are concerned. It is therefore necessary to have very long runs of any moulding to justify the use of the injection machine.

Moulds should be made from special mould steel and should be highly polished; they are sometimes chromium plated. They should be hardened, especially in those cases where inserts or loose parts have to be inserted or removed with the moulding, and replaced in the mould after each cycle. Large moulds have channels through which cold water may be passed if necessary. Maintenance of constant temperature of moulds is a critical factor in most production. It is clearly essential in order to maintain the right rhythm of production.

The mould is not always cooled. Depending on the nature of the material, it may be desirable to warm the mould. The necessary temperature conditions for each product can only be determined by trial. Adjustment of temperature and pressure enables the harder materials to be injected into a warm mould with the same time cycle as softer material would flow into a cold mould. In practice it is found that if the mould is not warm enough, there may be difficulty in filling it. The mouldings may be weak or fragile. If the mould is made too hot, the moulded pieces will tend to stick and may show shrinkage or distortion. The proper temperature range is determined by these two conditions.

The two parts of the mould are fitted on to platens. Unlike compression moulds, the two parts of the injection mould are held together by pressure before the moulding operation, and no space is provided for overflow or flash. The application of this holding pressure is one of the features on which much effort has been expended. Considerable internal pressures are developed, as much as 500 tons on large machines, and the clamping pressure must be capable of withstanding this. Usually an independent hydraulic system is employed to provide the necessary pressure.

So far as moulding conditions are concerned, to obtain the best results the following features have been emphasised, particularly in connection with metal inserts:

To obtain the greatest weld strength where hot plastic has to flow round the insert the necessary conditions are high cylinder and die temperatures, speed, and the use of preheated inserts. To obtain highest impact strength and best colour, a slow rate of injection, lower cylinder and die temperatures should be used. But to obtain best all-round characteristics and greatest strength, the best method is to avoid any welds, in other words, not to mould around the insert but to mould the solid article and drill the hole.

The common faults found in thermoplastic mouldings made by injection are *shorts*, *laminations*, and *depressions*.

Shorts occur when the mould is incompletely filled. This may be due to a cold mould, causing material to set in the channels. The mould is slightly warmed to overcome this trouble. A pocket of air may get trapped in the cavity, form an airlock, and prevent the plastic from completely filling the cavity. Air vents are normally present in the mould to prevent this.

If the injection temperature is too low clearly a higher pressure must be used to fill the mould. A moulding obtained by the injection process consists of a system of concentric layers formed by successive balloons of material being blown into the mould. If the injection temperature is too low, these balloons, when forced into the mould cavity, will not weld together, and will give an "onion skin" effect. Lamination of thermoplastic mouldings can be prevented by using the right temperature and pressure.

Injection mouldings sometimes show depressions. These appear when the material has been injected at too high a temperature. The material is too hot when it gets into the mould, and shrinks more than usual on cooling. The stresses set up result in the formation of sunken surfaces. The remedy is to lower the injection temperature.

REFERENCES

1 BUCHHOLZ. U.S.P. 1,810,126/1931.
2 EICHENGRÜN. B.P. 147,904/1920.
3 GASTROW. U.S.P. 2,057,945/1936.
4 HYATT. U.S.P. 133,229/1872.
5 MACHT, RAHM AND PAYNE. *Ind. Eng. Chem.*, 1941, **33**, 563.
6 PELOUZE. *See* Kline, *Modern Plastics*, 1940, August, p. 60.
7 SMITH. *Trans. P.I.*, 1947, p. 54.
8 ,, ,, B.X. Plastics, Ltd.
9 Photographs by courtesy of Alfred Herbert, Ltd.

CHAPTER XVII

ETHYL CELLULOSE

ETHYL Cellulose is of comparatively recent origin. It first appeared almost simultaneously at three sources: in 1912 it appeared in patent specifications taken out by Dreyfus,[4] Leuchs,[9] and by Lilienfeld[10] respectively. Though for some time comparatively little was done with it, yet in recent years it has assumed considerable importance. This has been most evident in the United States, although the activity in Germany is of longer standing. In this country we have been slow to become aware of its many admirable characteristics.

Ethyl cellulose has a number of characteristics which give it a great appeal for various applications, and it has advantages over the older better known cellulose esters such as cellulose nitrate and cellulose acetate. The outstanding features of ethyl cellulose may be summarised as:

(*a*) Excellent solubility in many cheap solvents.
(*b*) Compatability with plasticisers and oils.
(*c*) Compatibility with many natural and synthetic resins.
(*d*) Toughness and flexibility are retained through wide range of temperature.
(*e*) Inertness towards chemicals and corrosion.
(*f*) Heat and light stability.
(*g*) Excellent electrical properties.
(*h*) Thermoplastic character.

From the chemical point of view, it differs from these products inasmuch as it is an ether, whereas they are esters. For this reason it has greater chemical stability than cellulose nitrate or cellulose acetate. As a cellulose derivative it shares the typical cellulose characteristics. In particular, the different forms of sheet have great attractions. It is extremely flexible; it has great toughness; it is considerably more thermoplastic than the others; it has a lower water absorption than cellulose acetate, and it has the outstanding property of maintaining its strength and flexibility at very low temperatures. From the commercial angle it has advantages from the processing angle since it can be processed without employing solvents.

The Production of Ethyl Cellulose. Ethyl cellulose is manufactured from cotton linters or purified wood cellulose by the action of ethyl chloride or ethyl sulphate. It is the product which is obtained when an ethyl group replaces the hydrogen atoms in the reactive hydroxyl groupings in cellulose. The reaction need not be carried to completion as in the case of cellulose acetate, the substitution being partial according to the nature of the product desired. The extent to which substitution is carried determines the properties of the derivatives. The most effective types of ethyl cellulose are those containing between 2–2·5 ethoxyl groups in each glucose unit.

TABLE 94

VARIATION OF ETHYL CELLULOSE SOLUBILITY WITH SUBSTITUTION

Substitution Range Groups per Glucose Unit	*Solubility*
About 0–5	Alkali (4–8% NaOH)
0·8 to 1·3	Water
1·4 to 1·8	Increased swelling in polar (organic)—non-polar solvent mixtures
1·8 to 2·2	Increasing solubility in above
2·2 to 2·4	Increasing solubility in alcohol and less polar solvents
2·4 to 2·5	Maximum solubility
2·5 to 3·0	Rapid drop in alcohol, solubility, soluble inorganic non-polar solvents

The actual procedure is first to treat cellulose either as cotton linters or wood pulp with a strong solution of sodium hydroxide. This resembles the procedure in making viscose whereby alkali cellulose is formed. The alkali cellulose is then reacted with a strong alkylating agent, generally ethyl chloride. The ethyl group replaces the sodium in the alkali cellulose and forms ethyl cellulose.

The manufacturing conditions must be kept under very careful control. Alterations in the concentrations of reacting ingredients has a profound influence on the resulting material. The production is probably one of the most critical in the preparation of cellulose derivatives. Temperature conditions are maintained under careful control, so that undue degradation of the cellulose shall not occur. It is important, too, that there should be as great an economy as possible of alkylating agent which is comparatively expensive. The product is washed with large quantities of water in order to remove water soluble ingredients. It is then centrifuged and dried, finally appearing as fine white granules.

Some of the important factors involved in manufacture are illustrated in the following procedure described by Halm:[6]

Cellulose Ether Manufacture. In the manufacture of ethyl cellulose by reacting ethyl chloride with a suspension of cellulose under pressure, difficulty was formerly experienced in obtaining a uniform product owing to the uneven manner in which the cellulose (e.g. cotton linters) was penetrated by the ethylating agent. This defect can be remedied by starting from a less voluminous material in the shape of granulated cellulose pulp board which is impregnated, before ethylation, with a wetting agent. The resulting ethyl cellulose shows greater uniformity throughout the batch and is eminently suitable for film manufacture. 100 parts granulated cellulose pulp board (a granule size of $\frac{1}{8}$ in. × $\frac{1}{8}$ in. × $\frac{1}{26}$ in. has been recommended for ethylation) were sprayed with 400 parts of an 0·5 per cent aqueous solution of the wetting agent known as Alkanol M (believed to be the sodium salt of a high molecular fatty acid). After drying to a water content of 3 per cent the impregnated cellulose was mixed with 392 parts caustic soda, 180 parts water, 500 parts ethyl chloride and 813 parts benzene. The mixture was gradually heated to 150° C. in an autoclave and held at that temperature for 4 hours with constant agitation. The product was then cooled, washed with water, steam-distilled to remove volatile solvents and the residual ethyl-cellulose washed and dried.

The German process for manufacturing ethyl cellulose is carried out along the following lines: 54 kg. cellulose is kneaded for 4 hours with 600 kg. 50 per cent sodium hydroxide solution in a water-cooled stainless steel lined internal mixer. It is transferred to a stainless steel autoclave, where 210 kg. ethyl chloride is added with stirring. It is held 4 hours at 90° C., 7 hours at 110° C., and then brought up to 150° C. By-products and ethyl alcohol are distilled off. The remaining ethyl cellulose is washed numerous times, centrifuged, and dried. Their AT Cellulose contained 47–48 per cent ethoxyl and was soluble in benzene, alcohol, and 9:1 benzene-alcohol. AT Cellulose BS contained 42–43 per cent ethoxyl and was soluble only in benzene : alcohol 1 : 1 mixture.

According to Kraemer,[8] the molecular length of commercial ethyl cellulose corresponds to about 540 glucose units. This indicates a longer structure than exists with cellulose acetate, and implies that ethyl cellulose should be rather tougher than cellulose acetate.

Significance of Ethoxyl Content. A number of grades of ethyl cellulose are obtained according to the extent to which alkylation has been carried. The physical properties are greatly dependent on the ethoxyl content. Commercial materials are available in a number of different grades. Thus the Dow Company[3] markets two types defined as Standard and Medium; the Hercules Powder Company[7] actually prepares five types of ethyl cellulose.

The softening point of ethyl cellulose depends upon the ethoxyl content, thus as this becomes greater so the softening temperature becomes lower. Apart from this characteristic the more highly substituted materials containing between 48–49·5 per cent ethoxyl are more widely soluble in solvents, they have a higher water resistance, and are more compatible with other materials. On the other hand they are not as tough as the materials which contain lower proportions of ethoxyl.

It should be clearly realised that the ethoxyl content relates to the chemical composition. According to the conditions of manufacture, so the molecular length of the product can be varied. As a consequence the viscosity of a standard solution of ethyl cellulose can be influenced by this treatment since viscosity is a function of the molecular length. The viscosity will therefore vary, depending upon the mechanical treatment and the degree of degradation that has been permitted to take place during production.

Different Grades of Ethyl Cellulose. A number of grades of ethyl cellulose may be obtained according to the degree to which alkylation has been carried. These are differentiated by reference to the athoxyl content possessed by each type. For example, the Hercules Company markets five types,[7] as follows:

T—48·5—50% ethoxyl content
N—46·8—48·5% ethoxyl content
K—45·5—46–48% ethoxyl content
G—44·5—45·5% ethoxyl content
D—43·5—44·5% ethoxyl content

The Dow Chemical Co. markets the following types:

TABLE 95

SOFTENING POINTS OF ETHOCEL TYPES[3]

Ethoxyl Type	Ethoxyl Content		Softening Temp. °C.	Melting Temp. °C.
	Mols per C_5 unit	%		
Low . .	2·25–2·25	43·5–45·0	180–160	200–210
Medium . .	2·25–2·46	45·0–48·0	160–140	200–210
Standard .	2·46–2·58	48·0–49·5	140–160	200–210

Commercial materials are therefore available in a range of different viscosities, corresponding to each particular ethoxyl content. High viscosity materials will in general be employed for plastics, the lower viscosities being used for lacquers, and so on.

Properties of Ethyl Cellulose.[1] Ethyl cellulose has the lowest specific gravity of any of the commercial cellulose derivatives; its density is 1·14. Consequently it has a commercial advantage over the other materials. Ethyl cellulose softens at 140°C. and melts between 200° to 220°C.

Ethyl cellulose readily goes into solution in most solvents. Foils and films may be formed by casting its solutions. These foils and films possess exceptional toughness, and their strength is retained over a very wide range of temperature. The important fact is that even at extremely low temperatures, down to −70°F. ethyl cellulose films are extensible and resistent to shock. This is almost its most significant characteristic. Ethyl cellulose is unaffected by sunlight; it has remarkable stability towards heat.

These properties combine to make ethyl cellulose sheet attractive for laminated safety glass fixtures at very low temperatures.

Ethyl cellulose has exceptionally good electrical characteristics. It has high insulation strength and low specific inductive capacity, and also quite relatively low power factor. Thus foils of ethyl cellulose are extremely attractive as electrical insulating wrappings. In its plastic compositions, these properties are influenced materially by the presence of plasticisers. The significance of these properties is enhanced by the comparatively low water absorption which may be further improved by suitable compounding. Ethyl cellulose is unaffected by alkalis and dilute acids.

Ethyl cellulose is soluble in most organic liquids. So far as the high ethoxyl types are concerned, the only solvents which do not appear to affect it are straight-chain petroleum hydrocarbons. Ethyl cellulose of low ethyl content does not readily form solutions in many solvents.

Solutions in aromatic hydrocarbons, such as benzene, toluene, etc., are very viscous, and consequently cannot take up a high concentration of solid. It is found that the best types of solvents are mixtures of aromatic hydrocarbons with ethyl alcohol. Such mixtures give solutions having lower viscosity than either solvent gives individually. The best solvent combination comprises 70–80 parts of aromatic hydrocarbons, such as toluene or solvent naphtha, together with 30–20 parts of aliphatic alcohol such as ethyl alcohol. Such solutions are easy to make, and may be handled without difficulty.

The rapid drying characteristics of solutions of ethyl cellulose are very attractive. As a consequence, lacquers are utilised for application on various materials by dipping, roll coating, etc. Spraying lacquers are also made with comparative ease, and are quite satisfactory.

Compatibility with other Materials. Ethyl cellulose is compatible with many plasticisers and modifying agents. In actual practice comparatively few are used on any large scale.

Outstanding among the plasticisers are tributyl phosphate, tricresyl phosphate, and triphenyl phosphate. The chlorinated diphenyls are very effective. The whole range of phthalates work satisfactorily with ethyl cellulose. Apart from these, such materials as butyl stearate, amyl stearate, dibutyl sebacate, benzyl benzoate, sulphonamide plasticisers, etc., are all very effective.

TABLE 96

COMPATIBILITY OF N-TYPE ETHYL CELLULOSE WITH WAXES, TARS, AND SIMILAR COMPOUNDS

Compatible with	*Incompatible with*
Purified Montan Wax	Ceresin
Crude Montan Wax	Ozokerite
Beeswax	Paraffin
Candelilla Wax	Trinidad Asphalt
Japan Wax	
Spermaceti Wax	
Stearic Acid	
Oleic Acid	
Lauryl Alcohol	
Cetyl Alcohol	
Stearyl Alcohol	
Tallow	
Stearin Pitch	
Gilsonite	
Carnauba Wax	
Coal Tar	

In addition to these standard plasticisers ethyl cellulose is plasticised by all fatty acids, including castor oil, stearic acid, oleic acid, etc., and also by fatty alcohols, such as lauryl alcohol, cetyl alcohol, etc. Apart from these, the vegetable oils such as castor oil, linseed oil, cottonseed oil, and so on, are all compatible, and act as very effective plasticisers, either in the raw condition, or when blown. The bodied oils give harder materials than when the raw materials are used. The butyl esters and ricinoleic acid are also extremely useful in ethyl cellulose compositions. The ease of admixture shown by ethyl cellulose extends even further. It is extraordinarily compatible with many types of resins, and may be extended by their use. On the other hand it may modify the characteristics of the resins. For example, it is miscible with alkyd resins, many alcohol-soluble resins such as the natural resins and gums, rosin, phenol-formaldehyde resins, and so on. As a consequence it is used in varnishes to impart toughness, decrease tackiness and speed drying rates.

It is compatible in all proportions with cellulose nitrate, and many attractive mixtures have been prepared which give film of great flexibility and toughness.

One of the outstanding characteristics is the fact that it dissolves readily in hot resins, oils, waxes, and mixtures of these. By use of this property, compositions may be prepared which can be applied in the molten condition, and which form a basis for adhesives, coatings, and so on. With resins, plasticisers, and waxes, ethyl cellulose produces tough, waterproof, flexible adhesives for cloth, paper, and cellulose films, Heat-sealing adhesives without solvents can be made also with ethyl cellulose.

TABLE 97

EFFECT OF ETHYL CELLULOSE ADDITION ON MELTING POINT OF WAXES[7]

Composition %		Drop Melting Point °C.			
Wax	Ethyl Cellulose	Purified Montan Wax	Bleached Beeswax	Stearic Acid	Refined Coal-tar
100	—	69·5	62·5	55·0	27·5
90	10	86·5	103·5	56·0	88·0
75	25	115·0	144·0	71·0	118·0
66·7	33·3	117·5	—	87·0	132·0
50	50	134·5	182·0	114·0	171·0

Preparation of Ethyl Cellulose Plastics. By virtue of the ease with which it mixes with plasticisers, resins, waxes, etc., the conversion of ethyl cellulose into mouldable plastics is comparatively simple. It is achieved by mixing with plasticisers, either on open rolls, or in an internal mixer, such as the Banbury mixer. This procedure contrasts with the methods involving solvents used for nitro-cellulose and cellulose acetate which necessitates removing the solvents and lengthy storing procedures to eliminate residues. Shrinkage and warping are caused which have to be corrected. By contrast ethyl cellulose can be handled dry and there are none of the foregoing complications.

Comparatively high mixing temperatures must be employed, e.g. of the order of 150° C. Lower temperatures may be used, but mixing will take rather longer. Moulding compositions may be prepared with comparatively small quantities of plasticisers and added ingredients.

On the other hand, to obtain useful extrusion compounds, the proportion of plasticiser must be fairly high, e.g. exceeding 30 parts per 100 of ethyl cellulose. Mixing takes between fifteen to thirty minutes, depending on the amount of added material, and the temperature employed.

TABLE 98

ETHYL CELLULOSE COMPOSITIONS

(*a*)	Ethyl cellulose	100
	Chlorinated diphenyl	100
(*b*)	Ethyl cellulose	100
	Tricresyl phosphate	75
(*c*)	Ethyl cellulose	100
	White paraffin oil	40
(*d*)	Ethyl cellulose	100
	Raw castor oil	15
	Dibutyl phthalate	15
	White paraffin oil	25
	Titanium dioxide	1
	Oil-soluble red	0·3

TABLE 99

PROPERTIES OF ETHYL CELLULOSE PLASTICS

	Pure Film	Flexible Plastic
Density	1·14	1·05
Refractive index	1·47	1·50
Resistivity (ohms/cm.^{3})	10^{14}	10^{14}
Dielectric strength (volts/mil.)	1,500	750
Dielectric constant—		
25° C. 1,000 cycles	3·0	—
60 cycles	2·6	2·7
Power factor—		
25° C. 1,000 cycles	0·0025	—
60 cycles	0·0030	0·006
Tensile strength (lb./in.^{2})	8,000	3,000
Elongation (%)	15	90
Softening point	150° C.	80° C.
Melting point	200° C.	—
Water absorption (48 hrs. immersion)	4%	5·0%
Crack point	—	−55° C.

The usual procedure is adopted in mill mixing, that is to say, the mix is frequently cut, or else taken up on a scraper, so as to facilitate admixture. By virtue of its relative insensitivity to heat high temperatures may be employed with ethyl cellulose. For example, 200° C. may be used for mixing and handling such materials without adversely affecting the products.

Ethyl cellulose compositions are extensively used for extrusion purposes. By virtue of the excellent electrical characteristics, ethyl cellulose is used for insulation.

TABLE 100—PROPERTIES OF TYPICAL ETHYL CELLULOSE PLASTICS[11]

	Ethyl Cellulose A			Rubber	
	I	II	III	Dipped Article	Inner Tube
Water Absorption—					
Percentage of original weight after 24 hours	105·1	104·9	104·2	112·8	100·9
Percentage of original weight after 48 hours	105·3	111·5	104·9	115·3	101 1
Percentage of original weight after 70 hours	106·0	112·8	106·3	117·6	101·2
Dimensional Stability in Boiling Water—					
Percentage of original length after 10 minutes	98·0	99·5	—	102·0	100·0
Percentage of original width after 10 minutes	101·0	101·0	—	103·9	100·0
Percentage of original thickness after 10 minutes . . .	104·0	103·6	—	100·0	100·0
Appearance after removal from water	c	vh	—	Opaque initially	Opaque initially
Dimensional Stability in Water at Room Temperature—					
Percentage of original length after one week	102·4	107·6	—	110·0	101·0
Percentage of original width after one week	103·0	107·5	—	109·2	100·0
Percentage of original thickness after one week . . .	106·2	107·3	—	112·5	101·5
Shore Hardness—					
Shore values	31	29	27	Sample too thin	90
Tensile Strength—					
Pounds per cross-sectional sq. in.	1,700	1,170	2,290	4,500*	3,500*
Percentage Elongation . . .	103	86	123	760	575
Permanent Set—					
Percentage of total stretch retained from quick tension, 21° C. (Scott tester Dh-2) . . .	9	6	24·2	0	0
Percentage total stretch retained from slow tension, 21° C. .	11·5	81	—	0	0
Percentage total stretch retained from slow tension, 50° C. .	100	100	—	0	0
Flexibility at −20° C.:					
Number double folds (M.I.T. Flex Tester) . . .	170	No	97	65,000+	Sample too thick
Flexibility at Approximately −78° C. (Pinch test)	brittle	flexible	brittle	flexible	brittle
Burning Rate—					
Seconds for 3-in. lengths . .	71	78	—	02	66

Identification of materials tested: * Author's figures.

A-Ethyl cellulose, Grade "N" used (46·8 to 48·5 ethyl content, 100 centipoise viscosity).

Composition,

Col. I: Ethyl cellulose
Raw castor oil

Col. II: Ethyl cellulose
Cotton-seed oil
Raw castor oil

Col. III: Ethyl cellulose
Raw castor oil
Opal wax

High temperatures may be employed for extrusion, for example, die temperatures as high as 220° C. are commonly employed. Because high temperature can be used, and the material correspondingly becomes more fluid, very high rates of extrusion are possible, restricted only by the limitations of the haul-off equipment. For example, Du Pont de Nemours[5] suggest in one patent specification that speeds of extrusion up to 25,000 yards per hour have been attained, using temperatures up to 280°C. In the coating of wires with ethyl cellulose plastics, it has been found that advantages are gained by preheating wires. This has a very beneficial effect on the adhesion of the material to the wire, and the toughness of the covering.

Tubes, rods and sections of ethyl cellulose plastic are also made on a considerable scale for various applications. Straw-like extrusions have found considerable application for weaving into rattan-like materials employed for outdoor furniture, seats, etc.

Ethyl cellulose yields transparent plastic materials. As a consequence it is possible to obtain any range of colours and variation of colour effects by the addition of suitable dies or pigments in the mixing.

Plastic materials based on ethyl cellulose, apart from the factor of attractive appearance, are extremely tough, and when desired, very flexible. The characteristics are retained at quite low temperatures.

Rubber-like Compositions of Ethyl Cellulose. Plastic compositions containing fairly large proportions of suitable plasticisers give products having rubber-like characteristics. These are the materials referred to as "ethyl rubber." The plasticisers chiefly used for this purpose include castor oil, chlorinated diphenyl and various other similar materials. Thus tubes extruded with such materials are quite flexible, and for many purposes can replace vulcanised rubber. Water absorption of such materials is comparable with that of standard rubber compositions. The tensile strength is considerably higher, while the elongation is naturally only a fraction of the elongation given by rubber. On the other hand, it retains its mechanical characteristics down to very low temperatures, e.g. —70° C. This is a factor of outstanding importance particularly at the present time. It is likely to be an important factor in ordinary circumstances, not only in Arctic conditions, but also for general refrigeration purposes.

Ethyl Cellulose Plastics. Ethyl cellulose moulding powders are made by suitably compounding ethyl cellulose. Mixing is carried out as already described, but instead of the material remaining as sheet or strip, it is disintegrated to small granules. These moulding powders may be moulded by compression or preferably by injection moulding. When suitable compounded they have good flow characteristics, and yield tough mouldings having high gloss, good shock resistance, and excellent hardness.

A small proportion of lubricating material such as stearic acid is normally incorporated into moulding mixes. Rigid moulding materials may be prepared by incorporating filling materials into the mixes. The leading material used is zinc oxide, although the standard range of fillers may be incorporated without difficulty. The chief characteristic affected by the addition of fillers is the toughness and impact resistance.

TABLE 101

ETHYL CELLULOSE MOULDING POWDERS

Compression Moulding Powder—Transparent

Ethyl cellulose	100 parts
Chlorinated diphenyl	15 parts
Stearic acid	2 parts

Compression Moulding Powder—Coloured

Ethyl cellulose	100 parts
Dibutyl phthalate	12 parts
Triphenyl phosphate	12 parts
Zinc oxide	40 parts
Stearic acid	2 parts
Dyestuff	1 part

Injecting Moulding Powder

Ethyl cellulose	100 parts
Dibutyl phthalate	10 parts
Liquid paraffin	10 parts
Zinc oxide	30 parts
Stearic acid	2 parts
Colour	1 part

Compression moulding is usually carried out at about 150° C., with a pressure between ½ ton and 2 tons per sq. inch. It is, of course, essential to chill the moulding prior to removal. Ethyl cellulose suitably compounded is admirably suitable for injection moulding. Temperatures between 190–220° C., and pressures from 2 up to 15 tons per sq. inch are employed. Mould shrinkage is of the order of 0·005 inches per inch. The excellent flow characteristics show up to very good advantage. The mouldings come away quite quite readily from the moulds, without sticking, which is very desirable. Transparent products may be prepared, or the whole range of moulded coloured articles.

Such mouldings have excellent properties. They have very slight tendency for cold flow and they can be made flexible. They stand up to cold water, but soften in hot water. These materials begin to distort at a temperature of 60° C., although the true softening point is very much higher. They are extremely stable and stand up to heating at 200° C. for long periods without effect.

They are very tough and flexible and have excellent electrical properties.

TABLE 102

ELECTRICAL PROPERTIES OF ETHYL CELLULOSE PLASTIC COMPOSITIONS

Ethyl Cellulose	100
Mineral Oil	60

Heat distortion temperature	58° C.
Impact strength (Izod)	7·0 ft. lb. per in. of notch
Tensile strength	2,000 lb./in.^{2}
Elongation	70%

	20° C.	50° C.	75° C.
Dielectric constant, 1,000 cycles	3·0	2·9	2·75
Power factor, 1,000 cycles	0·0065	0·006	0·0055

Articles made from ethyl cellulose have good dimensional stability, which they retain under variable conditions of humidity. In view of the high electrical characteristics they are well suited for electrical applications.

Thus the electrical properties tend to improve with rise in temperature. Although ethyl cellulose compositions tend to take up a certain amount of water on prolonged immersion, yet the electrical properties are not greatly affected. Of equal importance is the fact that immersion at elevated temperatures does not ruin these electrical properties.

TABLE 103

ELECTRICAL PROPERTIES OF ETHYL CELLULOSE AFTER IMMERSION IN WATER

	Dry at 20° C.	48 hours at 20° C.	48 hours at 50° C.	48 hours at 75° C.
Dielectric constant, 1,000 cycles	3·0	3·3	3·5	3·6
Power factor, 1,000 cycles	0·0065	0·0078	0·0085	·0093
Water absorption	—	2·4%	5%	7%

Application of Ethyl Cellulose. The low temperature characteristics of ethyl cellulose have led to its use for aircraft purposes. For example, it has been applied for making laminated materials for use as aircraft components. In the rubber field suitable compositions have been employed in the production of raincoats, hospital sheetings, surgical tape and coated fabrics generally.

Ethyl cellulose products lend themselves well to fabrication. They may be handled by all the usual procedures employing wood or metal tools. The only complication is due to the thermoplastic character of the material, so that where excessive heat is developed there may be a tendency to stick to the tool. Bearing this in mind it may be sawn, drilled, turned, cut, etc., at will.

It is fairly evident from the wide solubility of ethyl cellulose that it can readily be made to adhere, so that composite articles can be made up. The material may be buffed and polished to give a very high gloss.

Ethyl cellulose has excellent compatibility with nitro-cellulose. Combinations of these, together with castor oil as plasticiser, provide the basis for a new artificial leather coating. The outstanding feature is that this artificial leather retains its toughness and flexibility at very low temperatures.

Low temperature shock resistance makes it most suited for glass substitute, e.g. in laminated glass, for use at low temperature, e.g. —40°C. Even polyvinyl butyrals are not suitable at such temperatures.

Ethyl Cellulose as a Casting Material. The outstanding heat stability and inherent toughness of ethyl cellulose has been utilised to the full in its most recent application as a casting plastic. A number of special proprietory compositions have been evolved. Thermocast is a typical one.[2] It combines several desirable features; good flow characteristics when molten; it retains exact mould dimensions; it has good durability; it is tough and acid-resisting. It becomes molten at a temperature of about 200°C., and may then be poured into simple moulds. Its leading application at present is in the production of metal forming tools and jigs.

The material looks like red sealing wax, but is much tougher and less brittle. It has high mechanical strength and is able to stand up to the pressures of the hydraulic press, pressures of three tons per sq. inch. Because it is thermoplastic the material has one outstanding advantage over other casting plastics. When a tool has been spoiled, it can be cut up, re-melted and re-used without any appreciable deterioration in physical properties. This is an important consideration allowing greater flexibility in changing tool designs when necessary.

A composition which is considered to be suitable for such casting processes is the following:

TABLE 104

ETHYL CELLULOSE CASTING MATERIAL

Ethyl cellulose	33
Hydrogenated methyl abietate	20
Pentalyn G.	15
Red iron oxide	20
High melting wax (180° F.)	10
Diphenylamine	1

The composition burns slowly only by direct application of flame.

Castings are made along the following lines:

Small pieces of the material are melted in a suitably heated container equipped with a sturdy stirrer, the temperature being maintained at 200° C. It is then cast into metal moulds, or suitably coated wood or plaster moulds. It is interesting that shrinkage only occurs on the open face of the mould, which may be subsequently machined down to size.

The temperature of the mould should be reduced gradually and held at 60–70° C., over a 24- to 48-hour period before reducing to room temperature, and conform closely to mould dimensions. Any type of cutting tool used at slow speeds can be employed to machine and trim the castings.

TABLE 105

PROPERTIES OF THERMO-CAST

	Possible Range
Specific gravity	1·18–1·28
Softening point (A.S.T.M.-ring/ball)	140°–170° C.
Pouring temperature	190°–215° C.
Hardness-Brinell (100 kg./15 sec.)	2·75–12·15
Compressive strength (to failure), lb./in.	5,000–12,000
Compressibility (under 1,500 p.s.i. load), in./in.	0·01–0·10
Impact strength—Izod (ft.-lb./in.^{2})	0·8–4·5
Cold mould shrinkage (in./in.)	0·001–0·006
Coefficient of thermal expansion (in./in. ° C.)	0·00005–0·0001
Tensile strength (p.s.i.)	800–3,300
Modulus of elasticity (p.s.i.)	50,000–100,000
Flexural strength (p.s.i.)	2,000–5,000
Water absorption (% 48 hr.)	0·22–0·35
Machinability	Very good
Castability	Excellent

REFERENCES

1 Bass and Goggin. American Soc. of Plastics, Lecture 13.10.1938.
2 Church. *British Plastics*, 1943, **15**, 396.
3 Dow Chemical Co. Technical Data.
4 Dreyfus. F.P. 462,274/1912.
5 Du Pont de Nemours. B.P. 538,716/1942.
6 Halm. U.S.P. 2,190,450/1939.
7 Hercules Powder Co. Technical Data.
8 Kraemer and Lansing. *J. Phys. Chem.*, 1935, **39**, 153.
9 Leuchs. G.P. 322,586/1922.
10 Lilienfeld. B.P. 12,854/1912.
11 Wiggam. *Modern Plastics*, 1942, **19**, 51.

PART IV

VINYL PLASTICS

CHAPTER XVIII

VINYL RESINS AND METHODS OF POLYMERISATION

THE plastics based on the vinyl resins constitute a large and growing family of increasing importance. They are also known as ethenoid resins. They are all based on the vinyl grouping. This chemical group is one of the most important "chemical bricks" available in synthetic chemistry. Chemicals containing the vinyl grouping have a remarkable aptitude for polymerising or joining up together into long chains. As the number of such units becomes larger, so resinous materials are formed, having plastic characteristics and acquiring very attractive physical properties.

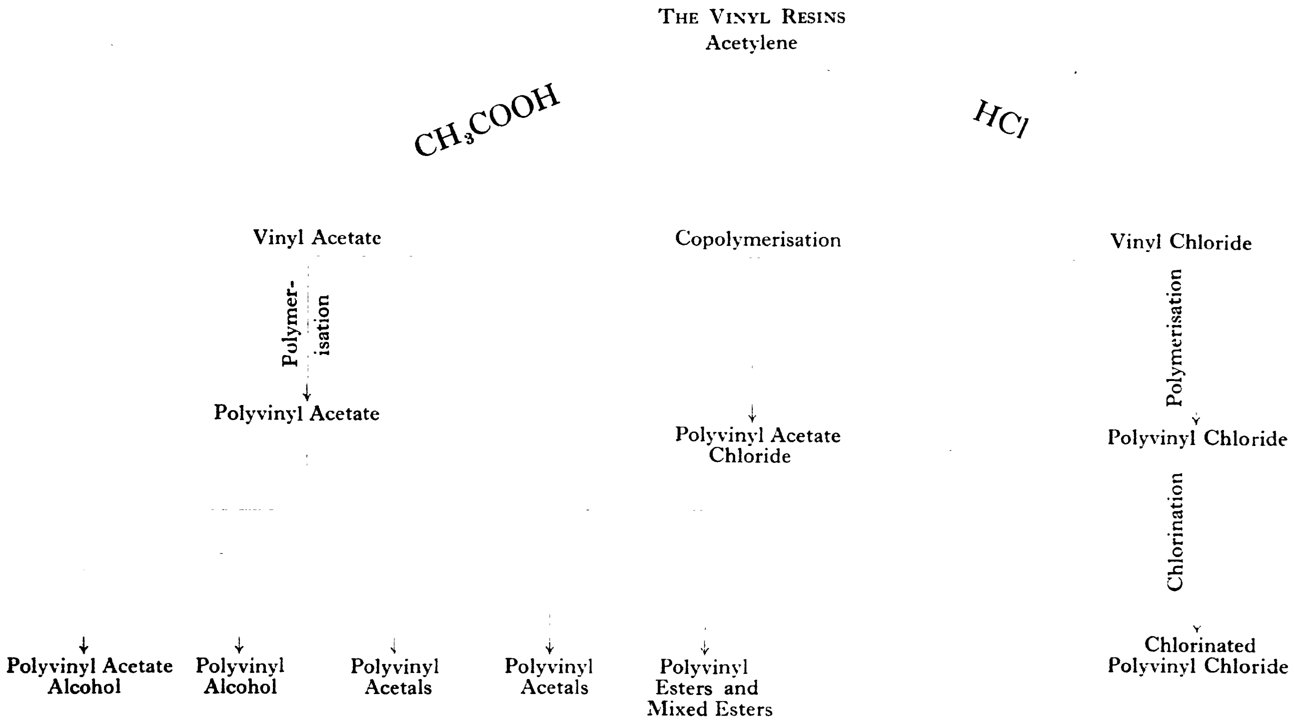
The vinyl resins are amongst the newest and yet the oldest synthetic resins. This paradox is easily explained. The chemical materials are amongst the oldest synthetic materials known; for the most part having been discovered over one hundred years ago. Outstanding examples include polyvinyl chloride, and polyvinylidene chloride. On the other hand, their appearance as materials of industrial importance is of comparatively recent origin.

The main properties which account for the applicability of these thermoplastics may be summarised as:

1. Stability to chemicals, more particularly towards oxidation, ageing, and metallic derivatives.
2. No taste and odour;
3. Good electrical characteristics;
4. High resistance to cold;
5. Simple processing properties;
6. High transparency.

The leading materials at the present time include polyvinyl alcohol, polyvinyl acetate, polyvinyl chloride, polystyrene, polyacrylic acid, polymethacrylic acid, and their esters, polyethylene, and an assortment of copolymers of these materials. There is a close relationship with other resins and rubber-like materials. The latter are based on the

TABLE 106—LEADING PLASTICS DERIVED FROM ACETYLENE

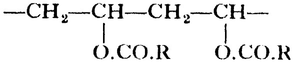
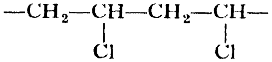
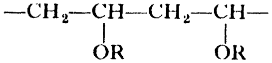
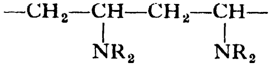
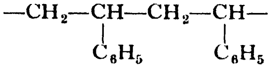
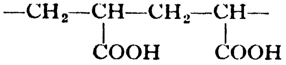
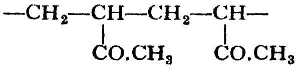


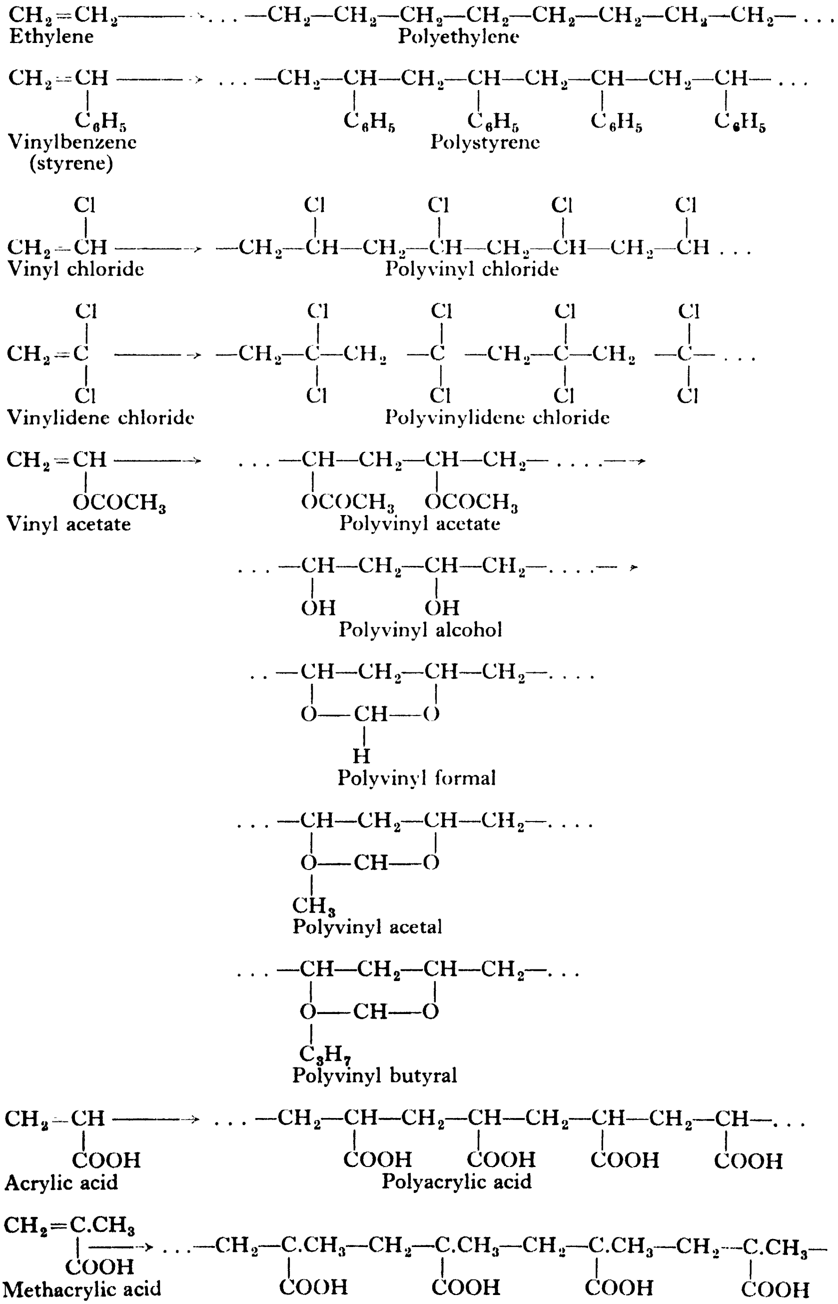
divinyl groups grouping where two vinyl groups are associated in close proximity. This illustrates the close association of this type of plastic with synthetic rubbers based on divinyl materials.

The preparation of plastics was in the first place based on polymers made from straight monomers. Thereafter it was found that copolymerisation of two or more monomers gave materials having interesting and novel characteristics. This trend has steadily grown and many copolymers are in wide use at the present time. The outstanding one is probably the copolymer of vinyl acetate and vinyl chloride. There is the further trend for the copolymerisation of vinyl materials with divinyl materials which finds its expression in the development of the latest types of synthetic rubbers.

TABLE 107

POLYMERISABLE VINYL DERIVATIVES FROM ACETYLENE

Addition Reaction	Vinyl Derivative	Part of Polymeric Structure
Acetylene (+Hydrogen CH – CH	Ethylene	$-CH_2-CH_2-CH_2-CH_2-$
+Fatty acids R.COOH	Vinyl esters $CH_2= CH.O.CO.R$	 $-CH_2-\underset{O.CO.R}{\underset{\vert}{CH}}-CH_2-\underset{O.CO.R}{\underset{\vert}{CH}}-$
+Hydrochloric acid HCl	Vinyl chloride $CH_2=CH.Cl$	 $-CH_2-\underset{Cl}{\underset{\vert}{CH}}-CH_2-\underset{Cl}{\underset{\vert}{CH}}-$
+Alcohols ROH	Vinyl ethers $CH_2=CH.OR$	 $-CH_2-\underset{OR}{\underset{\vert}{CH}}-CH_2-\underset{OR}{\underset{\vert}{CH}}-$
+Mercaptans RSH	Vinyl thioethers $CH_2=CH.SR$	 $-CH_2-\underset{SR}{\underset{\vert}{CH}}-CH_2-\underset{SR}{\underset{\vert}{CH}}-$
+Amines R_2NH	Vinyl amines $CH_2=CH.NR_2$	 $-CH_2-\underset{NR_2}{\underset{\vert}{CH}}-CH_2-\underset{NR_2}{\underset{\vert}{CH}}-$
+Benzene C_6H_6	Vinyl benzene (styrene) $CH_2=CH.C_6H_5$	 $-CH_2-\underset{C_6H_5}{\underset{\vert}{CH}}-CH_2-\underset{C_6H_5}{\underset{\vert}{CH}}-$
+Hydrogen cyanide HCN	Vinyl cyanide (acrylonitrile) $CH_2=CH.CN$	 $-CH_2-\underset{CN}{\underset{\vert}{CH}}-CH_2-\underset{CN}{\underset{\vert}{CH}}-$
	Vinyl carboxylic acid (acrylic acid) $CH_2=CH.COOH$	 $-CH_2-\underset{COOH}{\underset{\vert}{CH}}-CH_2-\underset{COOH}{\underset{\vert}{CH}}-$
+Acetylene CH=CH	Vinyl acetylene CH=CH.C—CH	
	Vinyl methyl ketone $CH_2=CH.CO.CH_3$	 $-CH_2-\underset{CO.CH_3}{\underset{\vert}{CH}}-CH_2-\underset{CO.CH_3}{\underset{\vert}{CH}}-$



$$CH_2{=}CH_2 \longrightarrow \ldots -CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2- \ldots$$

Ethylene — Polyethylene

$$CH_2{=}\underset{\overset{|}{C_6H_5}}{CH} \longrightarrow \ldots -CH_2-\underset{\overset{|}{C_6H_5}}{CH}-CH_2-\underset{\overset{|}{C_6H_5}}{CH}-CH_2-\underset{\overset{|}{C_6H_5}}{CH}-CH_2-\underset{\overset{|}{C_6H_5}}{CH}- \ldots$$

Vinylbenzene (styrene) — Polystyrene

$$CH_2{=}\overset{\underset{|}{Cl}}{CH} \longrightarrow -CH_2-\overset{\underset{|}{Cl}}{CH}-CH_2-\overset{\underset{|}{Cl}}{CH}-CH_2-\overset{\underset{|}{Cl}}{CH}-CH_2-\overset{\underset{|}{Cl}}{CH} \ldots$$

Vinyl chloride — Polyvinyl chloride

$$CH_2{=}\overset{\underset{|}{Cl}}{\underset{\overset{|}{Cl}}{C}} \longrightarrow -CH_2-\overset{\underset{|}{Cl}}{\underset{\overset{|}{Cl}}{C}}-CH_2\ -\overset{\underset{|}{Cl}}{\underset{\overset{|}{Cl}}{C}}\ -CH_2-\overset{\underset{|}{Cl}}{\underset{\overset{|}{Cl}}{C}}-CH_2\ -\overset{\underset{|}{Cl}}{\underset{\overset{|}{Cl}}{C}}- \ldots$$

Vinylidene chloride — Polyvinylidene chloride

$$CH_2{=}\underset{\overset{|}{OCOCH_3}}{CH} \longrightarrow \ldots -\underset{\overset{|}{OCOCH_3}}{CH}-CH_2-\underset{\overset{|}{OCOCH_3}}{CH}-CH_2- \ldots . \longrightarrow$$

Vinyl acetate — Polyvinyl acetate

$$\ldots -\underset{\overset{|}{OH}}{CH}-CH_2-\underset{\overset{|}{OH}}{CH}-CH_2- \ldots . \longrightarrow$$

Polyvinyl alcohol

$$\begin{array}{l}\ldots -CH-CH_2-CH-CH_2- \ldots \\ \quad\ \ | \qquad\qquad\quad | \\ \quad\ O-\underset{\overset{|}{H}}{CH}-O\end{array}$$

Polyvinyl formal

$$\begin{array}{l}\ldots -CH-CH_2-CH-CH_2- \ldots \\ \quad\ \ | \qquad\qquad\quad | \\ \quad\ O-CH-O \\ \qquad\ \ | \\ \qquad CH_3\end{array}$$

Polyvinyl acetal

$$\begin{array}{l}\ldots -CH-CH_2-CH-CH_2- \ldots \\ \quad\ \ | \qquad\qquad\quad | \\ \quad\ O-CH-O \\ \qquad\ \ | \\ \qquad C_3H_7\end{array}$$

Polyvinyl butyral

$$CH_2{=}\underset{\overset{|}{COOH}}{CH} \longrightarrow \ldots -CH_2-\underset{\overset{|}{COOH}}{CH}-CH_2-\underset{\overset{|}{COOH}}{CH}-CH_2-\underset{\overset{|}{COOH}}{CH}-CH_2-\underset{\overset{|}{COOH}}{CH}- \ldots$$

Acrylic acid — Polyacrylic acid

$$\underset{\overset{|}{COOH}}{CH_2{=}C.CH_3} \longrightarrow \ldots -CH_2-\underset{\overset{|}{COOH}}{C.CH_3}-CH_2-\underset{\overset{|}{COOH}}{C.CH_3}-CH_2-\underset{\overset{|}{COOH}}{C.CH_3}-CH_2-\underset{\overset{|}{COOH}}{C.CH_3}-$$

Methacrylic acid

Fig. 151. Leading vinyl products

The interest in vinyl compounds has opened up an entirely new field of chemistry. The chemical variations on the theme are being steadily worked out. Vinyl hydrocarbons such as styrene, vinyl alcohols, vinyl halides, vinyl esters, and so on, are comparatively familiar materials. But the chemical groupings tacked on to the fundamental vinyl group are growing in complexity and in number. So that vinyl compounds are now produced having, for example, heterocyclic groups attached.

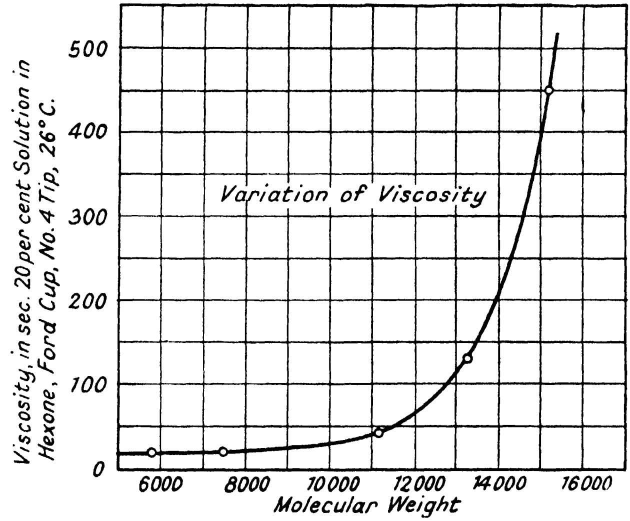


Fig. 152. Change of viscosity with molecular weight of polyvinyl-chloride-acetate[3]

This, of course, is all part of the ordinary chemistry of the vinyl compounds.

There are numerous sources of raw materials from which vinyl materials can be derived basically; they come from such products as coal, oil, natural gases, agricultural products, and so on. The fundamental key material is ethylene. It will be seen that in effect vinyl materials are substituted ethylenes, the physical properties of the products obtained depending upon the form of substitution. As already explained, ethylene may be obtained in prodigious quantities from the raw materials outlined above. As improved technique is developed both for gaining and handling ethylene and its derivatives, so the scope of the vinyl plastics will increase, and the price will decrease steadily. The trend has already set in. During 1947 something like 180 million pounds of these materials were used in the United States alone.

The vinyl plastics have many properties in common. They are all extremely light, although in the case of chlorine-containing types, the high weight of chlorine offsets some of the lightness of the plastic. They are all materials of high transparency. They also form films with the greatest of ease and the availability of transparent films in almost every type is an outstanding feature. They are all thermoplastic; the extent varying with the composition of the material, being influenced naturally by the use of plasticisers. They all show marked elasticity under favourable conditions. They are all extremely tough and strong when suitably compounded. The technique for handling them is common to practically every polymer of the group. There are enormous industrial outlets for these materials; already polyvinyl chloride has an outstanding position in the field of insulation largely owing to the shortage of rubber during the war. Methyl methacrylate polymers dominate the field as transparent materials for use in aircraft. Polyvinyl formals are outstanding as wire insulation; polystyrene and polythene are the outstanding electrical materials, and so on. These activities have already assumed considerable dimensions; it can safely be said that these applications merely represent the fringe of what is possible, and enormous developments can be foreshadowed.

Curme and Douglas[3] have admirably shown the change of properties with increasing polymer length.

Methods of Polymerisation. Polymerisation is generally achieved by four main methods, namely:

1. Direct polymerisation of the monomer without a solvent, e.g. casting styrene or methyl methacrylate.
2. Polymerisation of the monomer in some solvent.
3. Polymerisation of the monomer dispersed in some immiscible solvent, e.g. styrene in water.
4. Polymerisation in the gaseous phase.

In each case usually some polymerisation catalyst is present, generally an oxidising agent such as benzoyl peroxide, hydrogen peroxide, and so forth. Polymerisation is promoted by heat, light, irradiation, or occurs spontaneously. When carried out in a gaseous phase polymerisation is also aided by pressure.

The first two types are both single phase, the systems being homogeneous liquids. The first method is still widely used in the production of synthetic resins, for example, in the polymerisation of styrene and methacrylic ester. The second method involving solvents is employed with vinyl chloride, styrene, and so on. Normally these processes are carried out at moderate temperatures up to 150° C., and at ordinary pressure. With isobutylene very low temperatures are customary. In some cases, notably ethylene, high pressures are employed.

For many years the first two methods were predominant, but recently the third type of procedure has overshadowed the others and seems destined to supersede them. It is usually referred to as *emulsion polymerisation*, because the immiscible solvent is generally water, and consequently, since most monomers are liquids, emulsions are formed. Moreover, with adequate precautions such as the presence of a protective colloid, the final product remains in the dispersed form, either as an emulsion, or dispersion, according to whether the polymer is liquid or solid.

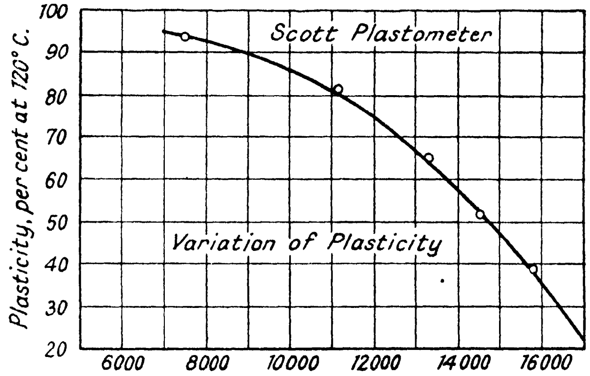


Fig. 153. Change of plasticity with molecular weight of polyvinyl-chloride-acetate[8]

In some instances as, for example, vinyl acetate, the monomer is soluble in water, and thus represents the second type of polymerisation. As polymerisation proceeds, the product may be insoluble in water, in which case this forms a dispersion, and the subsequent action is once again that of emulsion polymerisation.

The method adopted to carry out polymerisation has a profound effect on the properties of the ultimate product. Staudinger and Frost[19] have effectively demonstrated this by the work on the polymers obtained from styrene. They found that polymerisation in emulsion was much more rapid than polymerisation of pure styrene. The variations in molecular weights of the polymers were considerable.

When the commercial materials are considered, namely, the ethenoid plastics, it becomes quite evident that the most important method of production at the present time is that of emulsion polymerisation. Most large manufacture is based on this process. It also represents the most outstanding trend in plastics production at the present time. It heralds the transition from batch production to continuous production.

The Use of High Pressure. There has been a certain amount of interest in the influence of very high pressures on the polymerisation of diolefines, for polymerisation of conjugated diolefines occurs with a great decrease in volume, which would therefore be aided by pressure.

There has been an enormous amount of work on high-pressure polymerisation of ethylene. The main objective was to convert it into suitable fuels. But at least one outstanding commercial material with rubbery properties has emerged. This is the solid polymerised ethylene made by Imperial Chemical Industries (Plastics) Ltd.,[9] and known as *polythene.* It is prepared by heating ethylene at 100° C.–300° C. under a pressure of at least 1,200 atmospheres, when solid or semi-solid polymers are formed.

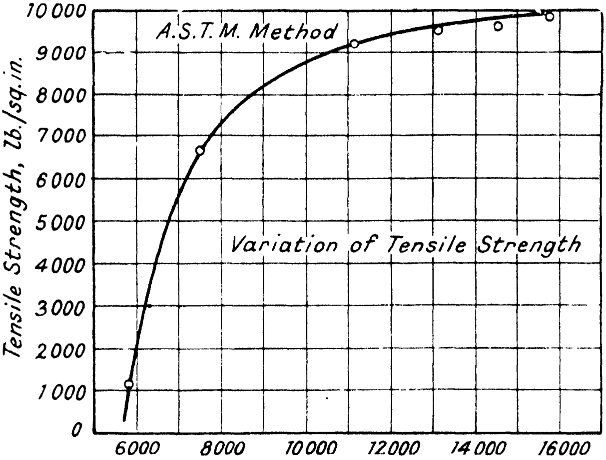


Fig. 154. Change of tensile strength with molecular weight of polyvinyl-chloride-acetate[3]

Polymerisation by Light. The effect of photochemical action on monomers is best brought out by its use in the case of polyvinyl chloride.

Regnault,[16] Baumann,[1] and Ostromislensky[13] used sunlight and ultra-violet rays to polymerise vinyl chloride.

According to Ostromislensky, the polymerisation was effected by irradiation from a mercury quartz lamp for twelve hours at 20° C.

Ostromislensky classified the resultant polymers as alpha-, beta-, gamma- and delta-, polyvinyl chlorides, according to solubility in acetone or chlorbenzol; α-polymer is soluble in acetone; β-polymer is soluble in chlorbenzol; γ- and δ-polymers are insoluble in chlorbenzol.

In the opinion of Ostromislensky, in the photo-polymerisation the process progresses with formation at first of α-polymer, which, under the continued action of ultra-violet rays, is converted into the β-form; the transformation of vinyl chloride into γ- and δ-polymers is conditioned by a further prolonged action of ultra-violet radiation.

In order to ensure a high degree of dispersion of polyvinyl chloride molecules the photochemical process, like the thermo-polymerisation may be conducted either in a solvent (e.g. alcohol, acetone, dichlorethane, etc.), or in emulsions.

The problem of photo-polymerisation of vinyl chloride in various solvents has been investigated by Plotnikoff,[15] and the colloidal properties of vinyl chloride polymers derived in different solutions were examined by Flumiani.[7]

The results of these researches showed that the speed of polymerisation of vinyl chloride in solution, at constant concentration, depends on the nature of the solvent, for example, the comparative values of polymerisation velocities in toluene is 1, in ethyl alcohol 25, and in carbon tetrachloride 68.

The effect of the ultra-violet rays upon the liquid vinyl chloride is so intense that the formation of polymers occurs almost spontaneously. It would seem, therefore, that out of numerous methods the photo-polymerisation of vinyl chloride has the most favourable chances of application, since it allows a continuous rapid procedure. There are certain difficulties of control which impede progress.

The Mechanism of Polymerisation. Melville[12] has summarised the information available about the mechanism of the combination of substances of high molecular weight. Considerable progress has been made in this branch of chemical kinetics. In general, high polymers are formed by polycondensation reaction or by the union of ethylene derivatives into chain-like molecules. The latter is the interesting type for consideration in the study of synthetic rubbers. In the case of ethylene derivatives considerable progress has been made because the reaction can be followed in the liquid and in the gaseous phase. According to Melville these reactions are substantially chain reactions. He stated that the derivatives most susceptible to polymerisation are the vinyl compounds of the general type $CH_2{:}CXY$. The substituent groups have a great influence on the course of the reaction. In general, the more highly polar X or Y is, the more readily is the polymer formed. The evidence that the reactions are of the chain type depends on the fact that small amounts of catalyst or of radiation will produce large amounts of the polymer. Yet these reactions are easily stopped by anti-oxidants. According to Melville the chain carrier is the growing polymer which is in a very reactive state. So that when it collides with a monomer molecule the latter adds on quite easily, involving a small amount of activating energy. When reactions are induced by addition of free radicals it seems clear that the growing polymer is simply a large, free radical with a terminal free valency. It is, however, difficult to explain by this mechanism alone such reactions as photo-polymerisation of chloroprene and of methyl methacrylate. Melville pointed out the striking property that these materials continue to polymerise in the dark, showing that the molecules exist for a long period. Another interesting feature is that these active molecules enable the development of heterogeneous polymers, so that it is possible to grow chloroprene on an active centre of polymethyl methacrylate. Since the action is subject to specific chemical inhibition it is probably chemical in nature. Melville stated that the structure of vinyl polymers has been established in several ways. By analogy with the behaviour of quite small molecules it seems that the predominating structure is of the head-to-tail type. X-ray evidence, too, in general, supports this opinion. Also the way atoms or groups may be removed, for example, chlorine from polyvinyl chloride, also tends to confirm this.

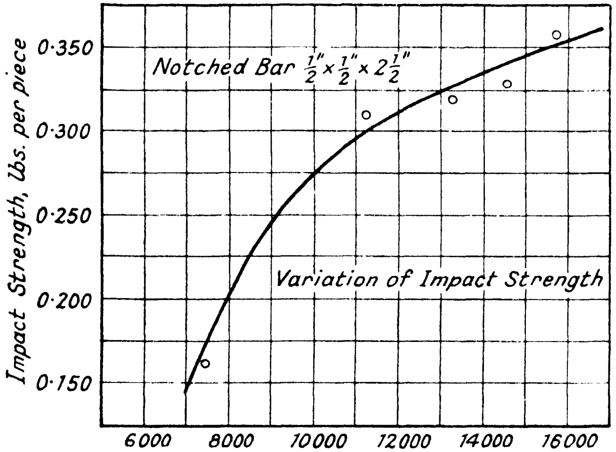


Fig. 155. Change of impact strength with molecular weight of polyvinyl-chloride-acetate[3]

Advantages of Emulsion Polymerisation. Polymerisation in aqueous emulsion has numerous overwhelming advantages over any other procedure, perhaps the most outstanding being that the reaction is always under control. There is little difficulty in handling the process and it may be stopped at any stage of the polymerisation. Equally important is the fact that the particle size can be controlled.

The end product is obtained as a very finely divided suspension or latex. With the presence of a suitable protective agent this can be rendered quite stable for an indefinite period. It is a simple matter to prepare dispersions which are at intermediate degrees of polymerisation.

The procedure lends itself to the addition of other materials, either to facilitate the actual polymerisation or to modify the properties of the subsequent synthetic material. The degree of polymerisation is necessarily determined by the nature of the treatment used, i.e. the temperature and nature of the catalyst, and the time involved. In general, the rate of polymerisation is much more rapid when this method is used. This may be a function of available surface.

One of the great features of all emulsion processes is the absence of solvents which are invariably either toxic, inflammable or expensive. The process works at quite low temperatures and reaction is smooth and under control, there being no violent surges or other uncontrollable reactions. As a consequence there are no deleterious resinous by-products formed. This has played an important part in synthetic rubber production. In fact, emulsion polymerisation eliminates most of the factors which have impeded particularly the commercial production of the synthetic resins and synthetic rubbers. This value is further enhanced by the fact that successive batches of material do not differ in their characteristics.

No difficulty is experienced in preparing monomers as emulsions. Very concentrated emulsions can be made, but 40 per cent monomer appears to be the most popular proportion. The final product is obtained as a finely divided suspension, or latex. The use of protective agents enables this to keep indefinitely. There is great scope for synthetic resins in the form of their respective latices, although little has yet been done in this direction.

All the familiar conditions associated with emulsions have been brought into play to deal with this problem of polymerisation, e.g. the use of emulsifying agents, protective colloids, electrolytes, etc. Superimposed upon the factors necessary for the straightforward emulsification has been the addition of catalysts to promote polymerisation, and also the addition of materials intended to modify the final products.

The nature of this emulsion is of great interest from two points of view. In the first place, the solid product may be obtained as in the case of rubber latex, by the addition of coagulating agents, such as acetic acid, formic acid, salts of polyvalent metals (such as aluminium sulphate), etc. Or alternatively it can be obtained as thin films by evaporation of the water which may be carried out as a continuous process. According to the degree of polymerisation, the films formed will vary from soft, semi-fluid materials to hard, glassy, solid products. In any event, the product lends itself to more easy purification than in the case of the lumpy materials obtained by other methods.

New Applications as Synthetic Latices. The second great advantage is that there is a wide field of application for the polymers as latices. This aspect has only lately acquired prominence. Products of this type have been on the market for a short time, and their uses are not fully appreciated. This aspect will be more fully dealt with.

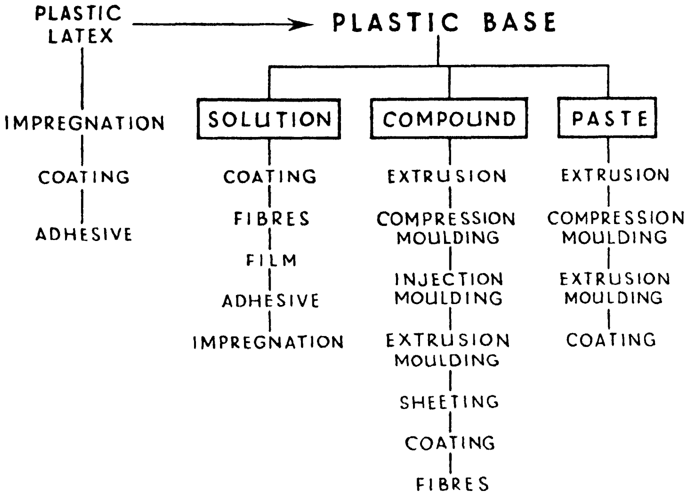


Fig. 156. Processing possibilities with vinyl resins

The scope of ethenoid plastics and synthetic rubbers has been greatly increased. For now they can be prepared as latices similar in many respects to rubber latex. They behave in a like manner. This has opened up new fields for their application. Rubber latex has its own sphere of uses as distinct from rubber in the solid form; in the same way plastic latices also have their own specific outlets. Moreover, in many cases they are replacing rubber latex.

In contrast to rubber latex films, dried-out films of these synthetic emulsions are resistant to oils, grease and many solvents, offering considerable scope for uses where ordinary latex or rubber solutions have proved quite unsatisfactory. Their films are generally very tough and nervy, while lacking the characteristic and often disadvantageous elasticity of rubber. These properties are dependent on the degree of polymerisation, the nature of the polymer, the presence of any plasticisers and other extraneous materials.

The ability of these polymer emulsions to hold fillers is extremely high, for they are quite stable. The loading capacity is far greater than the capacity of natural latex of equal concentration.

Complete freedom from smell and taste, combined with resistance to oil and grease, enable them to be used in contact with foods and beverages without any fear of taint.

A vast range of emulsifying agents has been employed in the production of synthetic resins. All the well-known soaps and wetting agents have been tried. Those most frequently encountered include sodium oleate, sodium stearate, a whole range of sulphonated mineral oils, organic sulphonic acids, saponin, etc.

The whole range of protective colloids, which include egg albumen, gum arabic, gelatin, glue, casein, milk, starch, dextrin, carrageen moss, are claimed to exert favourable effects on the emulsion, improving the stability during heat polymerisation and reducing the time required. Being water-soluble materials they tend to exert an unfavourable influence on the water-resisting qualities of the final product.

There are many other materials of every conceivable type which are claimed to have a good effect either on the polymerisation or on the properties of the final product.

The value of many of these additions is, to put it mildly, questionable. However, it is only now with production on a large scale in full operation that effective weeding-out of these materials is taking place.

TABLE 108

VARIATIONS IN MOLECULAR WEIGHT OF POLYMERS PRODUCED BY DIFFERENT POLYMERISATION METHODS[19]

Temperature of Polymerisation of Styrene °C.	Molecular Weights of Polymers	
	From Pure Styrene	From Styrene in Emulsion
30 . . .	600,000	750,000
60 . . .	350,000	400,000
100 . . .	120,000	175,000

Although polymerisation in emulsion can be carried out without catalysts, their addition greatly speeds up the reaction. The most important reagents employed, as in other forms of polymerisation, and for plastics generally, are the oxidising agents such as hydrogen peroxide, urea-peroxide, benzoyl peroxide, perborates, persulphates, percarbonates, ozonides, etc. Other types of catalysts include finely divided metallic oxides and salts of heavy metals, including manganese, lead, silver, nickel, cobalt and chromium.

Conditions for Emulsion Polymerisation. An excellent summary of the conditions required has been given by Mark and Rath.[11] A series of components (between five and ten) are needed to build up the colloidal system in which the polymerisation is expected to take place, and to start and direct the reaction to its proper ending.

1. *The basic phase*, in which the emulsion is made. This is always, or mostly, water (free from iron, lime, and organic impurities). It is always in excess and represents between 60 per cent and 80 per cent of the weight of the total system.

2. *The main monomer*—butadiene, vinyl chloride, etc.—to build up the backbone of the polymer to be produced. This will amount to about 60–80 per cent of the final polymer of 15–30 per cent of the emulsion.

3. *The additional monomers*—styrene, acrylic nitrile, acrylic esters, vinyl acetate, etc.—which are present only if copolymers are to be produced. These will represent 24–40 per cent of the weight of the final copolymer, or about 5–15 per cent of the initial colloidal system.

4. *The emulsifying agent* or agents, which enable us to produce colloidal dispersion of the monomers. Many different substances have been described and used, and it seems that the actual choice of a special emulgator is of a certain importance for the success of polymerisation. Aliphatic long-chain carboxylic and sulphonic acid salts, sulphonated long-chain alcohols and amines as well as aromatic alkylated sulphonic acid salts have been applied with success. 0·2–2·0 per cent of emulsifier, reckoned from the weight of the resultant polymer, are usually used.

5. *The stabiliser*, to prevent a premature precipitation of the emulsion. Various natural and synthetic protective colloids are recommended for this purpose, e.g. gelatine, flue, casein, starch, dextrines, methylcellulose, polyvinyl alcohol, etc. The usual amount of stabiliser is between 2 per cent and 5 per cent of the weight of the polymer.

6. *The regulator of surface tension.* the action of which cannot yet be clearly defined. It seems, however, that these substances have to be present to obtain and maintain the most favourable average particle size of the emulsion, and to narrow down as much as possible the distribution curve of the size of the dispersed particles of the monomer or the mixture of monomers. Aliphatic alcohols of medium chain-length, C_6 to C_8, seem to serve this purpose best, but aromatic alcohols and amines have also been recommended. They amount to between 0·1 per cent and 0·5 per cent of the polymer.

7. *The catalyst*, of which the main action is presumably the acceleration of the formation of polymerisation nuclei without affecting the propagation process. It seems, however, that most substances which

catalyse the starting reaction act similarly towards the cessation reaction and thus the addition of too much catalyst may result in a polymer of low molecular weight. Oxygen, ozone, hydrogen peroxide, organic peroxides and ozonides, persulphates, percarbonates, perborates and similar substances act as catalysts; they usually amount to between 0·1 per cent and 1·0 per cent of the weight of the resultant polymer.

8. *The regulator*, to direct the polyreaction and, presumably, to act mainly as an "anti-knocking" agent, avoiding or cutting down branching and cross-linking processes during the reaction. Very little is actually known about the action of these substances. Experience has shown that chlorinated aliphatic hydrocarbons such as carbon tetrachloride, ethylene dichloride, and hexachloroethene and similar aromatic compounds have a beneficial influence on the reaction, if about 2 to 5 per cent of the weight of the polymer is added.

9. *The* P_H *adjuster or buffer*. Most emulsions are very sensitive to the hydrogen ion concentration. The particle size and its distribution curve, the actual mechanism of the reaction and the stability of the final synthetic latex sometimes depend largely on the maintenance of the proper PH. Normal buffers such as phosphates, carbonates, acetates, etc., are usually applied in appropriate amounts (2–4 per cent of the weight of the polymer).

The above list shows that the mechanism of an emulsion polymerisation is quite complicated.

They considered the action of emulsion polymerisation to be polymerisation of the drops of the monomer proceeding inwards from the interface with the dispersion medium. Fikentscher[6] considered that the part dissolved in the aqueous solution polymerises, after which more was dissolved from the droplets. He based this on the fact that saturated solutions of vinyl monomers in water gradually formed emulsions of insoluble polymers. Staudinger[18] considered that polymerisation in emulsion strongly favours the formation of many activated spots on the surface of particles which give rise to a particularly reactive nucleus for promoting chain reactions and the process of polymerisation is therefore accelerated.

Some Disadvantages. There are a few disadvantages attached to emulsion polymerisation. These are all associated with the necessity for emulsifying agents and stabilising materials. Although present in small quantities, they are generally water-absorbing materials. In part they transmit a slight hygroscopicity to the finished product.

The dispersions can be made to yield almost clear, fine, regular powders, which are insoluble in water. The particles are different from those which may be obtained from solution, because they retain traces of emulsifying agents on drying, which hold firmly to small amounts of water. They are also somewhat more brittle and less resilient than when obtained from solvents. The structure of film cast from the dispersion is not so compact. In most cases a further slight heat treatment improves the transparency and the electrical properties by removing traces of water. It also seems to give a closer film packing.

In many instances the powders and films derived from these polymers may be too hard and inelastic. Just as compounding ingredients, plasticisers, colours, etc., may be added to rubber latex, so they may be added to emulsion polymers. They are added in the form of stabilised emulsions or dispersions.

The theme of emulsion polymerisation frequently crops up in the American patent literature. Thus Marks[5] proposed to prepare a dispersion of a polymerised organic compound in a liquid vehicle by emulsifying in a non-solvent liquid vehicle, the emulsion thereafter being flowed through a tube which is heated to induce polymerisation.

Another general method was disclosed by Röhm and Haas,[17] who polymerised unsaturated compounds having at least one vinyl group in the presence of a fine dispersion in water. The polymers were formed as small fine powders, the size of the grains being controllable. For example, 90 parts of vinyl acetate in 200 water containing 10 parts of talc and 0·5 per cent benzoyl peroxide were stirred for three hours at 80° C.

The advantages of emulsion polymerisation are further illustrated by the I.G. process.[8] In this they described the polymerisation of unsaturated compounds having the vinyl group, by using homeopolar polymeric compounds as emulsifying agents. Particularly useful are the neutral water-soluble derivatives of synthetic polymerisation products, such as polyvinyl alcohols which owe their solubility merely to hydroxyl groups. Not only is polymerisation facilitated, but frequently a much higher degree of polymerisation is reached. As an example, 150 parts of mono-vinyl acetylene and 350 parts of a 5 per cent aqueous solution of polyvinyl alcohol were heated for 20 hours at 100° C. with stirring. Polymerised vinyl acetate was produced in a finely dispersed form.

According to Plausen,[14] vinyl esters are first emulsified in water with an emulsifying agent having no chemical action on the products of polymerisation. The emulsion is then submitted to polymerisation.

Some of the General Properties of Dispersed Polymers. The degree of dispersion found in these emulsified polymers is very fine. With efficient stabilising agents regular dispersions are obtained, having particles less than 0·2μ in diameter. By comparison the size of the globules in rubber latex ranges between 0·5μ up to 3μ.

It has always been a drawback of the long chain compounds obtained by polymerisation that their solutions are extremely viscous. Beyond relatively small concentrations such solutions become unworkable. This is not the case with dispersions. One of the most useful properties of dispersed polymers is the low viscosity. The viscosity of dispersions is considerably lower than solutions of similar concentrations. The viscosity does not rise appreciably until concentrations of 50 per cent are reached.

Polymers of Acrylic and Methacrylic Acid Derivatives. In the field of polymerised derivatives of acrylic acid we come to the glass-clear, transparent plastics which have attained so much importance as substitutes for glass, notably in aviation, for scientific and technical use, for display and for moulding purposes.

This group includes such well-known materials as Perspex sheet and Diakon moulding powder, made by Imperial Chemical Industries, Ltd.; Lucite, made by Du Pont de Nemours, and Plexiglas, by Röhm and Haas—all of prime industrial importance.

These important plastics are being increasingly prepared by emulsification methods. The monomer is emulsified in water containing an emulsifying agent, such as sodium oleate and a catalyst of polymerisation. The emulsion is heated or exposed to light. The reaction may be stopped by addition of cold water, a circumstance which facilitates control of the process. Moulding powders of these plastics having exceptionally uniform particle size are being obtained from these emulsions.

Rate of Polymerisation of Vinyl Resins. Vinyl resins in general are prepared by polymerisation. The resin molecule consists of a linear chain in which the monomers have reacted with one another at the double bond to form high weight polymers. The reaction may be brought about by irradiation with ultra-violet light or by addition of a small amount of peroxide, ozone, or tetraethyl lead.

Vinyl compound polymerisation is a chain reaction in which a large number of molecules react in rapid sequence to form one macromolecule.[2] Polymerisation is influenced by several factors. For example, traces of certain impurities act as inhibitors and either retard the rate of polymerisation or lower the molecular weight of the resin formed, or both.

According to Douglas,[4] the rate of polymerisation varies directly as the square root of the catalyst concentration and doubles with every degree of 8°C. rise in temperature. It is also directly proportional to the concentration of the vinyl compounds present. In other words, solvent lowers the rate of polymerisation, and the amount of reduction is specific for each solvent. Average molecular weight, or degree of polymerisation of the resin produced, is directly proportional to the solvent concentration in the charge. Compounds that are solvents for the monomer but not for the polymer affect the molecular weight in the same way as do solvents for the average molecular weight. The latter decreases with increase in temperature and increase in catalyst concentration. The properties of the resulting resin are closely associated with its molecular weight and with the relative quantities of the various polymer bands of which the resin is composed.

Certain characteristics vary with the average molecular weight, others are independent of it. Thus tensile and impact strengths, abrasion resistance, and viscosity in solution increase, while water absorption, refractive index, hardness, and electrical properties remain practically constant. Solubility in organic solvents rises with decrease in molecular weight.

Vinylidene Chloride Polymers. Heat polymerisation of vinylidene chloride without added catalyst usually does not occur at a rate sufficiently high to be useful, but photopolymerisation has been successful both with and without auxiliary chemical catalysis. Light of wave length less than 4,500 Å. causes polymerisation at temperatures as low as −35°C.

In mass or bulk polymerisation, where only monomer and catalyst are present, the polymer is a flocculent percipitate below about 10 per cent conversion; between 10 and 20 per cent conversion the slurry becomes solid; above 20 per cent no liquid is visible, and the porous solid becomes harder with increasing polymerisation. With proper choice of conditions the reaction reaches 100 per cent conversion to polymer and results in the evolution of about 20,000 gram-calories per gram mol of monomer. To control the polymerisation rate and the physical characteristics of the product, it is often desirable to add to the monomer a solvent or an immiscible liquid and conduct the polymerisation in solution, emulsion or other dispersed system. The products of different polymerisation methods differ only in minor details.

REFERENCES

1 Baumann. *Ann.*, 1872, **163**, 308.
2 Carothers. *Ind. Eng. Chem.*, 1934, **26**, 30.
3 Curme and Douglas. *Ind. Eng. Chem.*, 1936, **28**, 1136.
4 Douglas. *Ind. Eng. Chem.*. 1936, **28**, 1125.

5 Du Pont de Nemours. B.P., 518,657/1940.
6 FIKENTSCHER. *Angew. Chem.*, 1938, **51**, 433.
7 FLUMIANI. *Koll. Zeit.*, 1928, **45**, 152.
8 I.G. Farbenindustrie. B.P. 406,173/1937.
9 Imperial Chemical Industries, Ltd. Technical data.
10 MARK. *Der Aufbau der hochpolymeren organischen Naturstoffe*, *Leipzig*, 1930.
11 MARK AND RATH. *High Polymer Reactions*, New York, 1941, p. 81.
12 MELVILLE. *J. Ind. Chem.*, 1942, Part 6, p. 264.
13 OSTROMISLENSKY. G.P. 264,123/1912.
14 PLAUSEN. U.S.P. 2,127,125/1938.
15 PLOTNIKOFF. *Z. wiss. Phot.*, 1922, **21**, 117.
16 REGNAULT. *Ann. Chem. Phys.*, 1838, **65**, 157.
17 Röhm and Haas Corp. B.P. 455,742/1933.
18 STAUDINGER. *Papier-fabr.*, 1938, **36**, 385.
19 STAUDINGER AND FROST. *Ber.*, 1935, **68**, 2351.

CHAPTER XIX

POLYETHYLENE

For many years a considerable amount of work has been carried out to convert ethylene into suitable motor fuel. Ethylene is a material which is widely available in refining gases, in natural gas, in coal gas, etc. It is also readily obtained by the dehydration of ethyl alcohol and is therefore freely available from numerous agricultural sources. Since ethylene is a gas it lent itself to work under high pressure and this was an angle that was freely exploited.

However, as a source for efficient cheap motor fuel, ethylene has not yet proved successful. One of the concerns interested in this field and very active in it was Imperial Chemical Industries, Ltd. Their technicians pursued the angle of subjecting ethylene to very high pressure, but also at very high temperature—an extremely difficult set of conditions presenting many chemical engineering problems.[3] They did not obtain motor fuel. But they did obtain a new plastic material—polymerised ethylene, which they called polythene and which now bears the trade name—*Alkathene.* Actually polythene refers to the group of solid materials thus available.

Fawcett[4] described the conditions of production in 1936. According to him polymerisation of ethylene under ordinary or slightly elevated pressure, or without catalysts, results in the formation of liquid products with molecular weight from 100 to 500. Only at 170° C. under a pressure of 1,000 atmospheres did the reaction yield a solid polymer with molecular weight of about 4,000. The use of temperatures up to 300° C. permits of the production of higher polymers with molecular weight up to 20,000. According to the leading patent, by Fawcett, Gibson, Paton, Perrin and Williams,[5] under these conditions, solid or semi-solid products are formed. The solid materials are resistant to water, acid and alkalis and can be formed into pliable, elastic, transparent films, and can be extruded. The reaction is strongly exothermic and quite rapid, requiring careful control. Conditions for production are stated to be 1,500 atmospheres pressure, temperatures between 150° and 250° C. and oxygen concentration of 0·08 per cent.

Polythene is of the greatest importance in the field of insulation, particularly for cables. It is an outstanding British contribution to the field of plastics. Production in the United States has been carried out by two concerns since 1942, and has already reached considerable proportions (about 15,000,000 pounds in 1947).[2] It has had a profound influence in many war applications. In its electrical properties it is almost as good as polystyrene, properties which are maintained at all frequencies. But polystyrene, as hitherto available, is rigid and somewhat brittle, consequently it cannot be used for applications where flexibility is required, e.g. as for cables. Polythene, by contrast, is horny and flexible, possessing just the right mechanical characteristics for such uses.

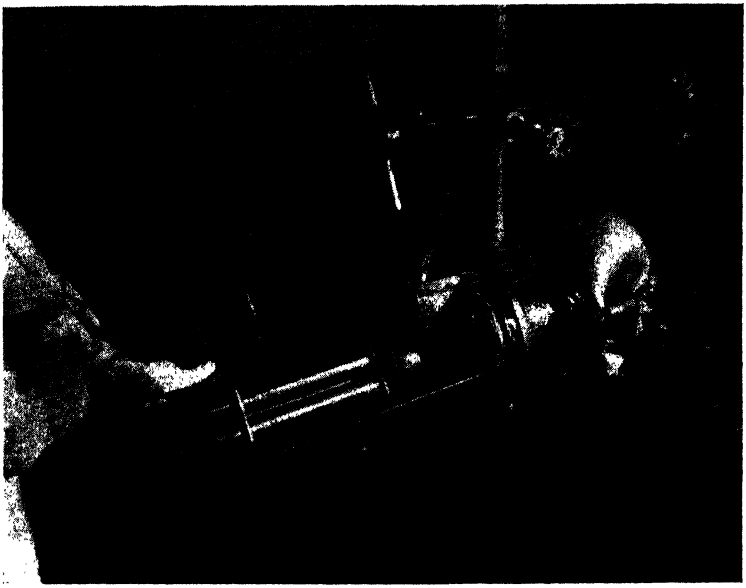
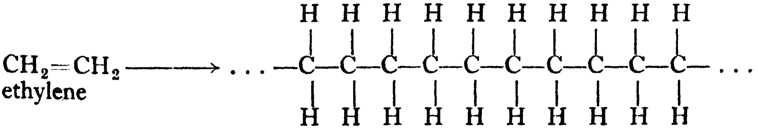


Fig. 157. Molten alkathene is injected into cooled copper moulds to form rods[9]

Properties of Polythene. Polythene is a white horn-like material with no odour or taste, having the very low specific gravity of 0·93. A number of polymers are available.

The polymers are long-chain hydrocarbons of high molecular weight. Sections of the hydrocarbon chain have the following chemical formula:



$$\underset{\text{ethylene}}{CH_2{=}CH_2} \longrightarrow \ldots -\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}- \ldots$$

It is almost a completely non-polar material.

Structure. Polythene consists mainly of crystalline material with some amorphous material as well. The crystalline part is made up of clusters of orthorhombic crystals radiating from a point (spherulites).

Polythene is a tough and flexible white translucent substance. In appearance it bears a close resemblance to paraffin wax. The outstanding disadvantage is that it can readily be scratched or cut, even by the thumbnail. Consequently where there is any chance of mechanical abuse it must be protected. The chemical inertness, water resistance and dielectric properties are all exceptionally good. The polymers are thermoplastic, and can readily be shaped by injection and compression moulding, extrusion, casting, etc. Rod, tube, tape, thin films and thread are all easily prepared, and with special technique polythene can also be used to impregnate or coat paper and all kinds of fabrics.

A number of types are available differing only in the degree of polymerisation.

The basis used for grading polythene is the measurement of the viscosity of the molten material at 190°C.

Physical and Mechanical Properties. The properties which vary with grade are shown in the Table below. The trend is towards the use of the tougher varieties.

TABLE 109

MECHANICAL PROPERTIES OF POLYTHENE

Material	Tensile Strength kgs./cm.^{2}	Ball and Ring Softening Point °C.	Approx. Viscosity Poises at 190°C.
"Alkathene" 2	160	115	35,000
"Alkathene" 7	140	112	10,000
"Alkathene" 20	120	110	3,500
"Alkathene" 70	100	106	1,000
"Alkathene" 200	80	100	350

The stress-strain diagram of polythene is very similar to that of gutta percha, and shows the phenomenon of "racking" or "cold drawing." Similar behaviour is shown by nylon and polyvinylidene chloride. When the tension reaches a certain value, an irreversible orientation and extension takes place up to about 400 per cent elongation. This elongation may be made partly reversible by heating to temperatures of about 100°C. This "cold drawing" is more marked in the more viscous grades of high degree of polymerisation.

Plasticity and Cold Flow. Above the softening point (about 115°C. for the hardest grade), polythene behaves as a very viscous liquid, and it is of interest that the softening point is much sharper than that of most thermoplastics being almost equivalent to a melting point. In this property it resembles nylon and polyvinylidene chloride, a fact also attributed to their crystalline structures.

Alkathene "20" at 100°C. is not particularly plastic, but at 106°C. is virtually a thick liquid.

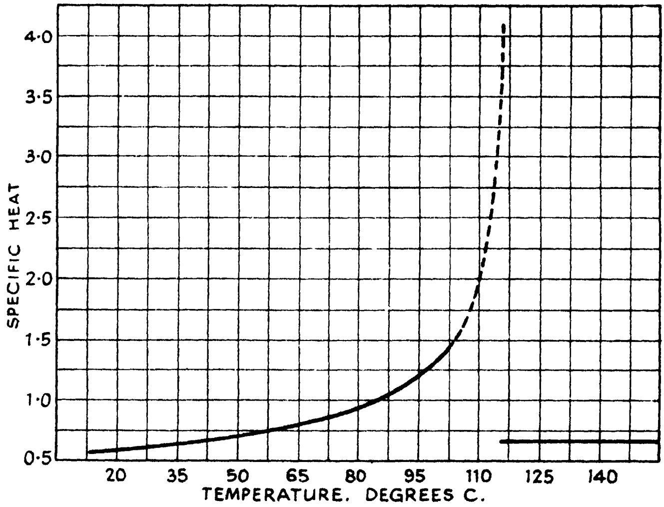


Fig. 158. Effect of temperature on specific heat of polythene

Below the softening point polythene is remarkably free from "cold flow." For example, a thin strip of Alkathene "20" after 120 hours at 40°C. under a tension of 14 lb./sq. inch showed zero permanent extension, while with the very high loading of 140 lb./sq. inch the permanent extension after a similar time was only 1·7 per cent. "Alkathene" 7 at 70°C. showed 7·8 per cent permanent extension after 120 hours loaded with 140 lb./sq. inch. Under compression the "cold flow" or "creep" is even less marked.

Flexibility and Brittleness. As the temperature is lowered, polythene gradually stiffens. The temperature at which it will crack is about —20°C. Plasticising the polythene with polyisobutylene reduces the cold cracking temperature, and if flexibility at very low temperatures is required 10 per cent or more polyisobutylene is added.

These properties guarantee for polythene a prominent position in the field of electronics.

Chemical Properties. All grades of polythene are practically insoluble in the cold in all solvents. At a temperature of about 60–70° C. they become readily soluble in the following solvents: benzene, xylene, toluene, trichlorethylene, carbon tetrachloride, chlor-benzene, petroleum ether (boiling point 80°–120° C.), tetrahydronaphthalene, turpentine, "medicinal paraffin," molten paraffin wax, and mineral lubricating oils. The relationship between solubility and temperature for xylene may be quoted as a typical example:

Fig. 159. Manufacture of "Alkathene" tape. Molten "Alkathene" is fed from a screw on to sheeting rolls[9]

Temperature	Solubility
20° C.	0·008%
68·5	0·25
69	0·96
78	10·2

Polythene is insoluble in water, ethyl and amyl alcohols, diethyl ether, glycerine, acetone, acetic acid, carbon disulphide and linseed oil.

Polythene is not wetted by water. In this respect, too, polythene resembles polystyrene and polyvinylidene chloride. Well moulded specimens show no gain in weight after seven days' immersion in water at all temperatures up to 100°C. Water absorption becomes detectable if the specimens are moulded at too low a temperature, figures of the order of 0·025 per cent gain in weight being found after seven days.

The rate of diffusion of water vapour through a film of polythene is approximately 0·4 mgs. of water/sq. inch/hour for a thickness of 0·03 mm. at room temperature, with 100 per cent humidity on one side and anhydrous calcium chloride on the other.

Fig. 160. Variation of density of polythene with temperature

Polythene has high resistance against corrosion. Thin strips of polythene are unaffected by immersion for one hour at 100°C. in concentrated nitric and hydrochloric acids, and in 50 per cent caustic soda. Concentrated sulphuric acid under the same conditions produces some charring. Prolonged exposure to some acids and to certain organic liquids such as alcohol may produce some surface cracking due to penetration of the crystal structure of the polythene.

Halogens are absorbed to a slight extent by polythene, although this does not affect its mechanical properties. It does permit halogens and sulphur to diffuse through it so that it offers no protection against these. It has excellent resistance against fluorine and hydrofluoric acid.

Lengthy exposure to bright sunlight does lead to some sort of breakdown because the material darkens and becomes somewhat brittle. Polythene shows no sharp absorption bands in the visible spectrum down to 2,200 Å, and only slight general absorption beginning at about 2,400 Å. It appears to be quite impervious to the action of ozone

TABLE 110

RESISTANCE OF POLYTHENE TO CHEMICAL REAGENTS (IN MASSIVE FORM)

Reagent	Behaviour of Polythene	
	Ordinary Temperatures.	High Temperatures
ACID AND ALKALI		
HCl HNO_3 H_2SO_4 Acetic Dilute (10%)	No action	No action at 100° C.
HCl (35 per cent)	No action	Slight absorption at 100° C. No effect on mechanical properties
HNO_3 (70 per cent)	No action	Oxidation and mechanical deterioration at 100° C.
H_2SO_4 (70 per cent)	No action	Discoloration at 100° C.
H_2SO_4 (98 per cent)	Slight discoloration of polythene and acid after some months. No mechanical deterioration	Discoloration and mechanical deterioration at 100° C.
Hydrofluoric acid	Very resistant. No mechanical deterioration	Resistant at 60° C.
Acetic (glacial)	Very slight absorption. Embrittlement of soft grade polythene	Some absorption (1 per cent at 60° C.)
$NaOH$ (40 per cent)	No action	No action
Aqueous salt solutions, e.g. brine, $CaCl_2$ solution	No action	No action

OXIDISING AGENTS		
Air	No action	No mechanical deterioration of solid at 100° C. Appreciable oxidation of liquid above 120° C.
Air and U.V. light (strong sunlight)	Very slow discoloration. No mechanical deterioration	Very slow oxidation in sunlight above 50° C. No mechanical deterioration
Ozone	Resistant. No mechanical deterioration	Oxidised in solution above 60° C.
Hydrogen peroxide (100 vol.)	No action. No effect on peroxide	Slow surface oxidation at 75° C.
Chromic acid (chromium-plating solution)	No action	No action at 40° C.
Chromic acid (pure CrO_3)	No action	No apparent action even on molten polythene at 120° C.
Potassium permanganate (acidified saturated solution)	No action	Slow oxidation at 75° C. No mechanical deterioration
HALOGENS		
Fluorine	Unusually resistant. No mechanical deterioration of massive solid	Some action and discoloration. No mechanical deterioration. Reacts in solution or as powder
Chlorine	Some absorption. Slight surface reaction. No mechanical deterioration of massive solid	Reacts
Bromine	Some absorption; slight surface reaction	Reaction at 75° C.
Iodine	Absorption and diffusion	Reaction at 100° C.
Sulphur	Slight absorption and slow diffusion. No reaction	Absorption and diffusion. No reaction at 100° C.

over long periods of time, e.g. 24 hours at 2 per cent concentration of ozone.

Polythene may be heated in an evacuated vessel at 290° C. for 100 hours, with no signs of decomposition. At 300° C. slight decomposition sets in. When heated in air, slight oxidation begins slowly at a temperature of about 120° C., and it is inadvisable to leave molten polythene in contact with air for long periods.

Prolonged heating or milling of polythene does result in oxidation which has disastrous effects on the electrical properties. To avoid this, small quantities of anti-oxidant are added.

Polythene can be ignited by a flame and will continue to burn slowly.

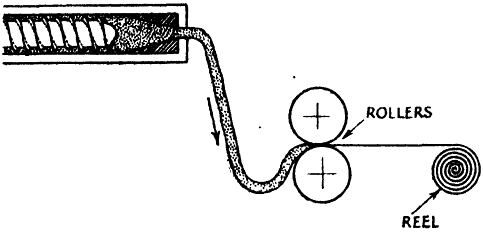


Fig. 164. Manufacture of polythene foil

Compounding. Polythene can be worked on heated rolls or in an internal mixer, provided that the temperature can be raised to at least 115° C. At this temperature the polythene softens and colours, etc., can easily be mixed in. Organic dyestuffs are normally used in quantities of from 0·1 to 1 per cent. In these small quantities they do not adversely affect electrical properties. Fillers may also be added, e.g. titanium dioxide, but the proportions should not be great or the polythene will tend to lose its toughness.

Carbon blacks tend to give some reinforcing effect with rather higher tensile strengths and greater stiffness.

Polythene is not compatible with many thermoplastics, but can be mixed with rubber, synthetic rubbers, gutta percha, polyisobutylene and paraffin wax. Mixtures with polyisobutylene are of particular interest since they have electrical properties which are almost identical with those of pure polythene, and the polyisobutylene has a plasticising effect giving a softer and more flexible product especially at low temperatures. Quantities up to 50 per cent may be added. Small amounts of paraffin wax, of the order of 15 per cent, may be added without seriously affecting the electrical or mechanical properties. The polyisobutylene mixtures have a wider plastic range than the pure polythene, a fact which is useful in the control of extrusion.

Tests on coloured polythene, containing 0·25 per cent of various organic dyestuffs, show no measurable deterioration in the electrical properties and the power factor is still only 0·0005 at 10^6 cycles.

Extrusion. Polythene can conveniently be extruded from the standard type of rubber screw-forcing machine.[8] Polythene is applied by extrusion for its leading application—high frequency cables. It is essential, however, that the barrel should be heated to at least 115°C., and die temperatures up to 160°C. will be required for extruding the stiffer grades. Recommended die temperatures are 130°C. for low polymers up to 160°C. for high polymers. Experience has shown that the most convenient method is to preheat the polythene to about 120°C. in an internal mixer, or on mixing rolls. The softened viscous polythene is then transferred to the extrusion machine which is preferably of the roller feed type. If the extrusion machines have not got separately heated heads, the temperature of the whole must be maintained at the recommended die temperatures. Then provided that the nip between the roller feed and the screw is kept well filled with the heated polythene, perfectly even extrusion will result.

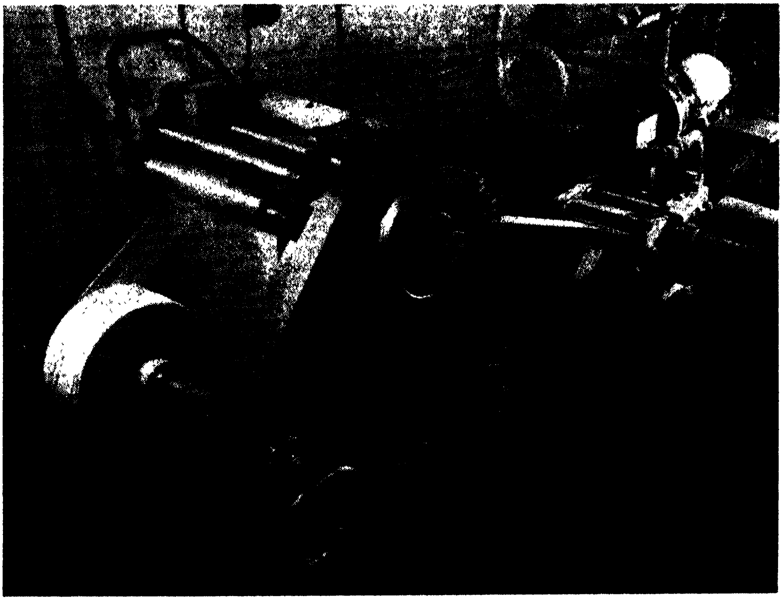


Fig. 162. Reeling off "Alkathene" tape[9]

The procedure developed for covering wire with unplasticised polythene to make a cable illustrates the technique. With modern plastic

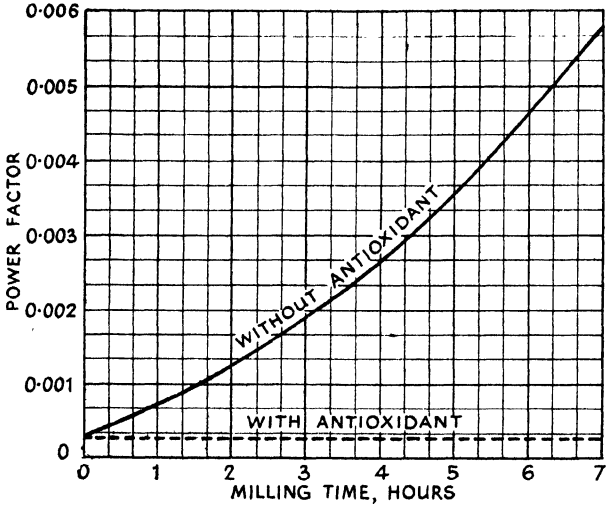


Fig. 163. Effect of milling time on power factor of polythene

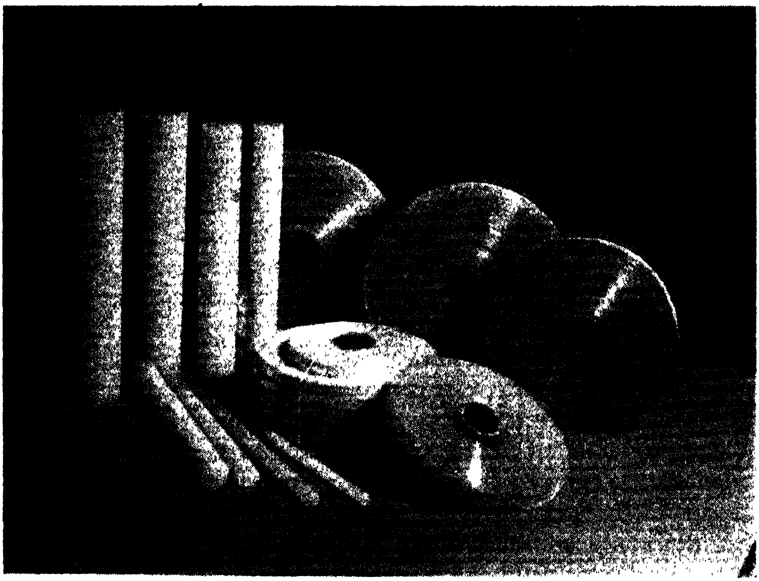


Fig. 164. "Alkathene" rods and tape[9]

extruders, the polythene can be fed cold. This is the normal American practice. The wire is preheated and fed at a uniform rate. The polythene in granular form is fed cold into the screw which may be cooled with water if necessary. Screens at the breaker-plate prevent the passage of lumps. The temperature of the throat, head, and die are carefully controlled, e.g. by circulation of oil. The freshly extruded material is cooled slowly, first in hot water, and then in cold water. This slow cooling is required because of the extremely high coefficient of thermal expansion of polythene. The decrease of volume in cooling from 120° to 20° C. is from 12 to 16 per cent, and more than half of this takes place during a rapid crystallisation between 120° and 80° C. Too rapid cooling would cause the surface of the coating to be hardened while the centre remains still soft. The decrease in volume during further cooling would result then in the formation of voids in the interior of the mass. Controlled cooling overcomes the difficulty and enables extrusion of heavy walls. Mixtures of polythene with polyisobutylene can be extruded with less care in the cooling because the exterior does not become so rigid when cooled.

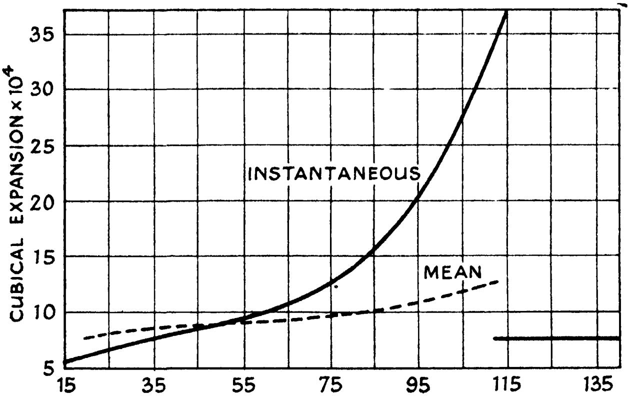


Fig. 165. Thermal coefficient of cubical expansion of polythene

The use of a low temperature at the die, e.g. 100° C., is not desirable as although the product may appear satisfactory, it will develop a tendency to go cheesy and brittle.

A common fault with unsuitable extruders giving rise to very irregular extrusion is the attempt to feed cold polythene or only partially softened material to the screw. In order to obtain satisfactory results, the temperature of the polythene fed to the machine, and the barrel, must be above 115° C.

Richards[7] has given the following data, obtained when cold-feeding Alkathene 2 to a 2-in. extruder:

TABLE 111

Temperature—Barrel, 140° C.; head, 160° C.; die, 175° C.
Screw speed—60 r.p.m.
Conductor—1/0·036.
Die diameter—0·075 in.
Haul-off rate (yds./hr.)—800, 2,000, 2,800, 3,200, 5,000.
Radial thickness of covering (inches)—0·060, 0·040, 0·035, 0·030, 0·012.

Grade	Extrusion Temperatures.					
	Hot Feed			Cold Feed		
	Barrel	Head	Die	Barrel	Head	Die
"Alkathene" 20 . .	115	130	135	135	145	150
"Alkathene" 7 . .	135	140	150	145	160	170
"Alkathene" 2 . .	140	160	175	155	180	195
Experimental Grade T .	160	190	210	180	215	230

Conditions for a 1¼-in. diameter screw covering a 3/0·029 conductor with 0·050 in. of polythene from a 0·165-in. die at 2,000 yards/hour.

Polythene mixtures, e.g. with polyisobutylene, can be extruded in a similar manner.

The extrusion product can be cooled either by water or by air.

Impregnation. Polythene can be emulsified, and the emulsions may be used for coating and impregnating cloth, etc.

Coating and impregnation from solutions is also possible, but it is important to evaporate the solvent above 110° C., as otherwise the polythene is deposited as a powder and not as a coherent film. Commercial xylene is a convenient solvent to use as its boiling point of 140° C. enables fairly rapid evaporation to be carried out at about 115° C.

Moulding. Polythene is very easily injection moulded, using a die temperature of from 160°–220° C. according to grade. In compression moulding it is important to reach a temperature of at least 115° C. Too low a temperature sometimes gives apparently satisfactory mouldings, which, however, rapidly become very brittle and cheesy. The shrinkage is high, averaging 0·018 inch/inch for injection moulds, and 0·011 inch/inch in a positive compression moulding.

It is satisfactorily moulded by compression in positive moulds. Because of the excessive thermal shrinkage, it is important to maintain the moulding under pressure during cooling.

The high polymers are specially suitable for mixing with waxes and its comparatively low viscosity makes it of value for impregnation purposes. It is not very suitable for moulding or extrusion.

The medium grades are used for most general purpose work, and are suitable for compounding with polyisobutylene.

The lower polymers have advantages in some types of extrusion work, e.g. in the production of tubing, especially when pure uncompounded polythene is used. They are also quite suitable for moulding.

Polythene may be sheeted by several methods. It can be calendered. It can be extruded as rod or sheet and rolled between cooled rollers. Or it can be sliced from blocks in very much the same way as the cellulose plastics are handled.

Polythene is a delightful material to machine and can readily be handled on woodworking or metal-working machinery.

Polythene films or pieces of polythene may be heat-sealed and welded without any difficulty although oxidation sometimes interferes.

Uses of Polythene. Polythene has the stability and inertness to chemical attack typical of the normal paraffins. This chemical stability combined with its toughness and flexibility over a wide temperature range, and the ease with which it can be moulded, extruded and formed into sheet, film or fibres (and hence fabrics) suggests a wide variety of uses as a coating or wrapping material. Because of its comparative rigidity in thick sections, it is suitable as a structural material for containers, pipes, and other equipment. The low density of polythene (0·92 at ordinary temperatures) is an important feature. Great economy in weight may be achieved by the use of polythene containers or polythene-lined drums for the transport of corrosive materials. In the fabrication of chemical equipment the ease with which polythene sections may be welded together is of great value.

The water vapour permeability of polythene is very low. It is one of the best waterproofing materials. Polythene film retains its good waterproofing properties up to high temperatures, after severe creasing and after prolonged exposure to moisture. Polythene film is comparable with rubber hydrochloride and moisture proofed regenerated cellulose film, and is vastly superior to polystyrene, rubber, and cellulose esters.

Polythene film was used with great success during the war for protecting mepacrine tablets in the tropics.

Paper or cardboard coated or impregnated with polythene also has a low water vapour permeability, and polythene may be added to wax for use in waterproofing paper, in order to raise the softening-point and to improve the crease resistance of the proofed paper.

Extrusion of Tubes. Extruded polythene tubes are made in a wide range of sizes for use as electrical sleevings, and conveyor pipes for chemicals. A typical field of application is in the brewing industry. A 2-in. screw machine is capable of making tubes from 0·125 to 2 in. outside diameters, with wall thicknesses varying from 0·005 to 0·25 in.

The extruded tube must be drawn off from the die to prevent sag and distortion. The most convenient manner of cooling is to pass the tube through a short air-cooling tube placed about 3 in. from the extrusion die. During cooling a stream of air is passed through the tube from the extruder.

A convenient manner of producing thin films of polythene of Grades 2 to 70 is to extrude through a narrow slit orifice, and to pass the film between a pair of cooling rolls. Films 0·002 to 0·020 in. thick may be successfully manufactured from a single 1¼ in. screw, using either hot or cold feed.

To maintain a perfectly uniform film, careful control of extrusion conditions is necessary. Normally, the extrusion is made oversize, and both the fall to the rolls and the setting of their nip are adjusted to produce the required thickness. The film may show marked "grain" effects due to orientation.

Compression Moulding. Compression moulding is used for moulding sheets and very simple shapes. Low pressure is necessary during the heating, but should be increased as cooling proceeds. To prevent voids, especially in thick sections, the cooling must be slow, and it is important that one face of the moulding be cooled at a slower rate than the other.

Typical conditions for moulding 1-in. thick, void-free slabs of polythene on a 250-ton press are 150° C. for Alkathene 20 and 7, and 160° C. for Alkathene 2. The heating time is usually 20 to 30 minutes and the cooling cycle 15 minutes.

Injection Moulding. Polythene is admirably suited for injection moulding. The nozzle should be the hottest part of the machine, so that the polythene is most fluid just before entering the injection gate.

High temperatures are preferable where flow is restricted due to narrow cavities or inserts. To avoid excessive flash in these cases, pressures of 1,000 to 2,000 lb. per sq. in. are usually sufficient.

It is important to apply a follow-up pressure during cooling to prevent voids. As the material first in the mould contracts further polythene must be available to take up the volume difference, and so on until the moulding is complete.

Extrusion Moulding. In extrusion moulding polythene is forced into a mould by a screw-type extruder. The mould is clamped against the extruder nozzle and filled with molten polythene until it emerges from air vents, which should be placed at corners remote from the filling nozzle. When the mould is filled the air vents are sealed and the mould cooled down. To prevent voids due to thermal contraction, the mould is cooled progressively from the parts farthest from the filling nozzle, at the same time maintaining a small flow of polythene from the extruder. Large mouldings may be made in this way.

Hot Melt Coating. Polythene is an efficient moisture-proofing agent for paper. Treated papers show high resistance to water vapour permeability even after creasing. They may be heat sealed and are particularly useful for fabricating foodstuff containers, waterproof wrappings, and tropical packs.

Micro-crystalline or amorphous waxes are preferred because of their relatively high softening points and good flexibility. Typical recipes for paper coating are 20 parts "Alkathene" 70 with 80 parts amorphous wax, or 30 parts "Alkathene" 200 and 70 parts wax.

The polythene or polythene-wax mixture is heated to 100° to 120° C. in a bath fitted with a partly submerged metal roller over which is mounted a heated "doctor" or scraper knife. Paper is drawn through between the roller and knife, and the thickness of coating is controlled by the viscosity of the mixture, setting and temperature of the doctor knife and speed of draw-through.

Films of 0·0005 to 0·003 in. thick have been applied to tissue, kraft, and manila papers.

Melt Flowing and Casting. Some types of polythene are especially suitable for simple casting techniques. "Alkathene" 200 is preferred because of its free flowing melt at 140° to 150° C.

Hollow articles such as beakers, bottles, and flasks may all be made on sheet metal formers. The mould is first coated with a lubricant and filled with the required amount of cold polythene, which is then heated to about 140° C. The mould is then inverted so that the polythene runs down the sides and forms a smooth, complete layer. After cooling in water, the casting can be removed very easily. Various thicknesses may be produced by varying the temperature and time of draining.

Simple articles such as carboy caps, gasket and sealing rings may also be made by dipping metal formers into molten polythene bitumen mixture and then allowed to drain before shock cooling. Any number of coats may be applied to build up the required thickness, each single coat preferably being $\frac{3}{32}$ in. or less. A particularly useful mixture for dipping is 85 per cent Alkalthene 200 and 15 per cent bitumen at 160° C. The products are tough and withstand rough treatment.

Powder Spraying. A specially prepared fine powder may be sprayed through a gun of the type made by the Schori Metallising Co.

The powder is blown through a concentric flame of an ignited mixture of air and butane or boosted town gas. The article to be sprayed should be warmed and the polythene coat subsequently "flamed" to give a smooth uniform surface. Thick coats and large surfaces should also be annealed at 100° C. to release strains induced during cooling. Heating to 200°–250° C. for a few minutes oxidises and toughens the polythene and improves the bond to the metal.

Polythene sheets and tubes of all grades may be jointed by hot gas welding. A stream of nitrogen at 200° C. is directed on to the joint and a polythene filler rod used to make the weld. In this way large containers for corrosive acids, pipes 3 to 4 ft. in diameter, T-pieces, flanged pipes, etc., may all be fabricated speedily and cleanly.

Sheet may be manipulated at a temperature about 105° C. by bending and shaping over formers or by blowing with air at a pressure below 5 lb. per sq. in. Tubes may also be bent at about 105° C.

In all cases of shaping, the degree of bending should be greater than that ultimately required, in order to counteract slight reversible extension effects. Precautions must also be taken to complete the manipulation while the polythene is at 105° C. and to maintain the desired shape until the article has completely cooled.

Polythene may be machined very easily, using ordinary wood-cutting tools and moderately high speeds; an air blast directed at the turning helps to keep the polythene cool and removes swarf. Machining presents a simple and speedy means of making prototypes for service evaluations of Alkathene for the many new uses that are already being developed.

Electric Properties. The electrical characteristics of polythene are quite outstanding, especially since the material is so flexible. They account for most of the application of the material. Measurements of the electrical properties have been made by a large number of different workers, and the figures given below are average values.

TABLE 112

ELECTRICAL CHARACTERISTICS

Dielectric Constant	2·3 at 20° C. and all frequencies between 50 and 5×10^7 cycles/sec. There is a tendency for the dielectric constant to fall with increasing temperature, e.g. to 2·0 at 100° C.
Power Factor	0·0005 at all frequencies between 50 and 5×10^7 cycles/sec.
Volume Resistivity	10^{17} ohms/cm.^{3}
Surface Resistivity	10^{14} ohms/cm.^{2}
Breakdown Voltage	1,000 volts/mil.

Polythene has played such an important part in electrical insulation that it is well worth considering the implications of electrical requirements.

Outstanding Requirements of Electrical Insulating Materials. The life of electrical equipment is controlled by the life of insulation. The chemical stability of insulating materials is of a much lower order than that of conductors so that electrical breakdown nearly always occurs in the insulation. The trend is for equipment to withstand greater electrical stresses working at higher temperatures. This involves continual improvement in insulating materials.

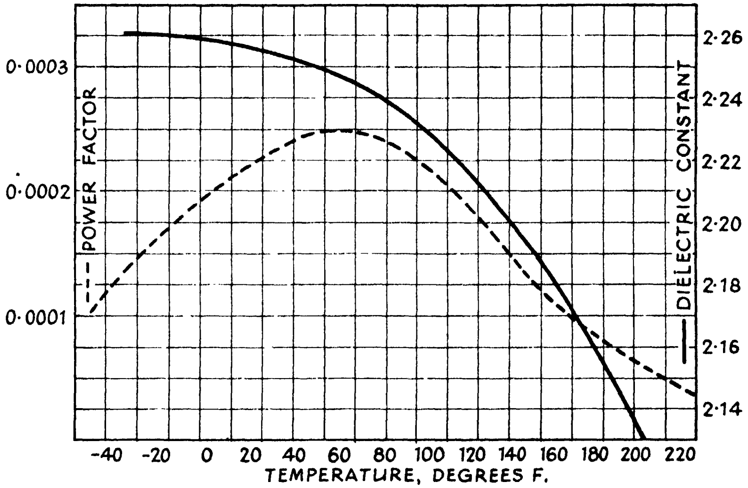


Fig. 166. Effect of temperature on dielectric constant and power factor of polythene

In recent times plastics such as polythene, polystyrene and polyisobutylene, have played an outstanding part in solving insulating problems. It should be noted that these are all hydrocarbons and non-polar. Other materials such as phenol-formaldehyde plastics, ethyl cellulose, polyvinyl chloride, cellulose acetate, and so on, all of them polar to some extent, all play important parts in electrical equipment. It is therefore desirable to consider some of the important factors concerned.

Polar materials contain polar groups. This term applies to such radicals as $—OH$, $—COOH$, $—CHO$, $—CN$, $—CONH_2$, $—SH_2$, $—NH_2$, $—NHCH_3$, $—NCS$, $—COR$, $—COOR$, $—NO_2$, $—CH{=}CH_2$, $—C{\equiv}CH$, and groups containing oxygen, nitrogen, sulphur, chlorine, etc. Such materials will all have a certain affinity for water. Plastics containing these groups will have such affinity to a greater or less degree depending on their structures.

Massey[6] has outlined the four fundamental properties of insulating materials as (*a*) conductivity, (*b*) permittivity, (*c*) dielectric loss, and (*d*) electrical strength.

Conductivity. The application of electromotive force to a material causes a flow to the electrodes of any charged particles which may be free to move. This is, of course, the electric current. The fewer the free particles present (as is the case in high polymers) the less the current. Conductivity of metals is independent of voltage and decreases with rise in temperature. In dielectrics, rise in temperature or the voltage increases conductivity by promoting molecular breakdown. This applies to plastic materials. The converse of conductivity is *resistivity*, which is generally given in terms of the surface or of the volume of the dielectric material concerned.

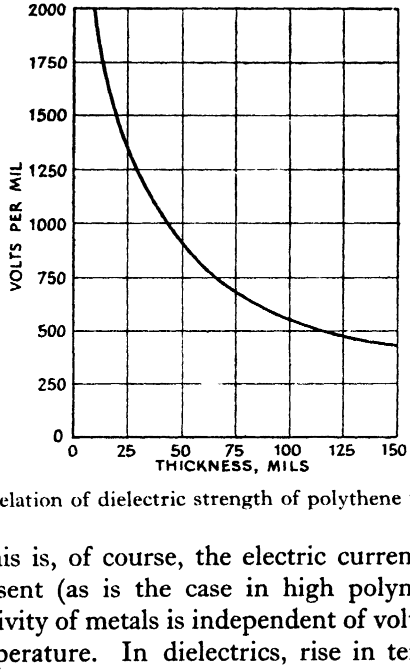


Fig. 167. Relation of dielectric strength of polythene to thickness

Permittivity. This is also known as the dielectric constant or the specific inductive capacity. Apart from any free charged particles are the bound charged particles which can be elastically displaced by an electromotive force and the movement of these particles during deformation and relaxation constitutes a flow of electric charge. So that by arranging two electrodes separated by a dielectric, electricity can be stored under a steady potential, or, alternatively, transmitted from a source of alternating potential. This set-up is a condenser. The amount of electricity stored or transmitted varies with the electrical displacement of the bound particles. The magnitude of this property in any material is called the permittivity or dielectric constant.

Dielectric Loss. The movement of charged particles in the dielectric of a condenser is resisted by external force, so that any displacement takes place with the development of heat. Energy converted into heat is no longer electrical and is lost. This is called the dielectric loss. The amount of this loss is indicated by the value known as power factor. This is the ratio of the current associated with the energy absorbed as heat to the total current supplied to the condenser. It is usually desirable that dielectric materials should have very low power factor. Actually, it is not always a matter of great significance. Power factor is affected by temperature and by the frequency of the alternating current.

Electric Strength. The limiting value of electromotive force gives the measure of the breakdown voltage. The voltage gradient is the electric strength. The usual breakdown in commercial insulating material starts at local weak spots and impurities. These impurities of high dielectric loss when subjected to an alternating field will rapidly reach a temperature which may cause vaporisation and lead to breakdown.

So the electrical properties of dielectric materials may be summarised as conductivity (or resistivity) which depends on the presence of free charged particles; permittivity which is due to bound charged particles; dielectric loss being the energy lost as heat; and electric strength which is the resistance to rupture by an electric field.

Correlation of Electrical and Chemical Properties. Massey has made it clear that a search for new and better insulating materials involves consideration of the electrical structure of atoms, valency links, molecules, and chemical groups. This is one more example of the profound scientific background of plastics.

Molecular complexity in solids usually favours high electric strength, low conductivity, and low dielectric constant by limiting the movement of particles. This is evident by consideration of the long macromolecules of plastics meshed together.

In general it can be stated that polar materials, or the presence of polar groupings, tend to result in unsatisfactory electrical properties. By contrast the non-polar materials such as hydrocarbons tend to have good electrical properties.

The reactions involved in plastics formation, i.e. polymerisation and condensation, lead to the production of a long chain or a cross-linked stable electrically desirable structure. In many cases, for example, phenol and formaldehyde, the starting-off materials are polar, mobile, and electrically bad. The electrical properties depend entirely on the degree of conversion to resin. However, the formation of water in condensation processes is a source of many electrical troubles, and every precaution is taken to eliminate such moisture in the use of these resins. The presence of trapped water in highly stressed dielectrics is a serious fault.

Thermoplastic Dielectrics. This is one of the reasons why so much attention has been paid to polymerisation resins such as polythene, polystyrene, methyl methacrylate, etc., which are formed without any production of water. These resins are, of course, thermoplastic, and unfortunately the softening points are not yet far enough removed from operating temperatures of electrical equipment. Nevertheless they have superb electrical properties and are extensively used.

While polythene is flexible, polystyrene is rigid, tending to be brittle, and cannot be used for flexible insulation. In such cases plasticisers are added to confer flexibility. It is not yet fully realised that the electrical characteristics of such mixtures are often more influenced by the mobile plasticiser than by the resin itself. This is quite evident to those who have worked with polyvinyl chloride compositions.

Effect of Impurities. This leads to a major aspect of insulation. The suitability of any plastic material, however good in itself, will depend upon its freedom from impurities. Dielectrics (i.e. plastics) must be free from water and any other polar liquids such as acetone and alcohol; for if they are uniformly dispersed through the solid dielectric they may render it conducting. In any event they give it polar properties and affect power factor, dielectric constant, and electric strength. If they are present only as occluded drops they do not affect conductivity. They may, however, lead to increase in power factor and permittivity. In a material of poor heat conductivity the heat generated may be sufficient to cause the adjacent dielectric to decompose leading to electric breakdown.

The importance of water in dielectrics, i.e. in plastics, is outstanding. Any water must be eliminated from the finished product. Moreover, good insulating materials should have not only a low water absorption, but also low permeability to water vapour. Insulating materials to be subjected to high electrical stresses must also be free from non-polar solvents, such as benzene, for example. Such solvents may volatilise to form gas pockets leading to ionisation and rapid breakdown.

A dielectric should not contain trapped air or voids of any sort, since ionisation is caused under comparatively low electrical stresses, much lower than the solid material can withstand. In such cases heat is generated and thermal breakdown of the surrounding plastic may occur.

In an unfilled resin or plastic such as polythene, any fibrous impurities are objectionable because they either hold or attract moisture and form conducting paths. Quite evidently one does not use solid conducting particles in an insulating material. Even non-conducting impurities can adversely affect the electrical properties if they have a permittivity greatly different from that of the plastic used. This is because a small particle of low permittivity may take an excessive part of the stress, thus acting as a weak spot and leading to breakdown.

Where fillers are used with plastic insulating materials the same considerations already outlined must apply. They must be free from electrolytes and any liquids; moreover, there should not be any pronounced difference in dielectric constant between filler and the binder material. The mixing procedure and other processes must not introduce any voids. The solvents employed to help the mixing must be completely removed. Any fibrous fillers employed must be carefully dried before being used.

This brief summary gives some indication of the difficulties associated with processing plastics which are to be used for electrical purposes.

Until the last few years the greatest emphasis was on the use of the thermosetting resins for electrical purposes. Their importance still grows. It is a fact that at least 90 per cent of the resins used in the electrical industry are still based on phenol-formaldehyde. The outstanding electrical properties, accompanied by chemical stability, dimensional stability, and insolubility of the final products, is obtained with materials which are easy to handle.

However, latterly materials such as polythene, polystyrene, etc., have opened up new possibilities for electrical equipment which has not hitherto been available. The design of equipment and its performance may quite well be revolutionised by the availability and use of these and other plastics. Communications during the present war have already been profoundly affected.

Substitution among Materials used for Cable Insulation. A considerable proportion of the development work in recent years aimed at improving insulation, particularly on wires and cables, has been concerned with these synthetic materials.[1] In fact, much of the progress of synthetics has been due to this work on insulation. While comparatively few have the high electrical characteristics necessary for insulation, many others are excellent for protective sheathings.

One of the great problems of substitution during the war was to replace rubber. Hitherto in this instance the urge had been to overcome the unsatisfactory properties of rubber. Rubber often requires external protection which takes the form either of treated fabric or of a lead

TABLE 113

DESCRIPTIVE CLASSIFICATION OF LEADING TYPES OF INSULATION

Descriptive Classification	*Base or Mixture*
Arc-resisting	Hydraulic cement and asbestos
Flame-proof	Impregnated hydraulic cements
Heat-resisting High frequency	Lead borate and mica
Hot service (up to 110° C.) Superior electrical	Phenol and vacuum dried fillers
Normal electrical	Phenol and selected wood fillers
Impact-proof	Synthetic resin and large flaked fabric
Impact-resisting	Synthetic resin and small flaked fabric or cotton
Good stability	Synthetic resin and mineral fillers
Large insert	Synthetic resin and special fillers
General purpose	Cresol synthetic resin and wood fillers
Multi-coloured (dark) shades	Phenol, cresol, and urea resin mixtures
Moderate temperatures (up to 60° C.)	
Ultra-high frequency	Polythene, polystyrene
Superior electrical	Polyvinyl chloride Cellulose acetate Ethyl cellulose Rubber mixtures
Normal electrical	Shellac, bitumen, waxes
Low loss	Polystyrene, polythene
Multi-coloured	Methyl methacrylate and fillers
Opaque	Urea resin and wood Urea resin, mineral and paper
Translucent	Urea resin and alpha cellulose
Transparent	Methyl methacrylate Methyl methacrylate Glycerol phthalate Phenol resins (cast)
Normal temperatures	Bitumens, pitches (up to 30° C.) waxes

coating. Both these types of protection have disadvantages. Fabrics are subject to rotting, and other forms of destruction, white lead, apart from the weight aspect, is susceptible to corrosion.

Another great problem is to find substitutes for silk, paper, and cotton, which is also coupled with the necessity for obtaining improved performance. Another aspect is the urgent need to replace various drying oils and natural resins in lacquers and varnishes, a search which is also bound up with the desirability for improved performance.

TABLE 114

ELECTRICAL CHARACTERISTICS OF SUPER DIELECTRICS (COMPARED WITH PURE RUBBER)

	Polyisobutylene	Polystyrene	Polythene	Rubber
S.G.	0·91	1·05	0·93	0·91
Dielectric Constant. 60 cycles	2·3	2·5	2·3	2·37
Breakdown v. per m. . .	600	700	1000	1000
Volume Resistivity, ohms/cm.^{3}	10^{15}	10^{17}	10^{17}	10^{17}
Power Factor 1,000 cycles .	0·0004	0·00015	0·0005	0·0016

A brief survey of the position may best be made by considering four main fields of cable insulation: high voltage, medium voltage, low voltage and high frequency. Many materials have sufficiently good characteristics to find application in more than one field of cable insulation.

Substitution in the High Tension Field. In the field of power transmission, for cables working at high voltages, substitution of the materials used for many years has not yet progressed very rapidly. Ceramic insulation and air are the leading forms of insulation for overhead lines, while underground cables still consist, in the main, of stranded copper conductors, surrounded by numerous layers of paper, the whole system after vacuum treatment, being impregnated with mineral oil. The cable is sheathed in lead. Chief requirements called for are low dielectric loss and high dielectric strength. The main urge for substitution in this instance is the desire for a more simplified, direct form of production. Relatively few synthetic materials have the requisite characteristics.

Polystyrene, polythene, and polyisobutylene are the leading materials that have been considered. They are all hydrocarbon polymers with extremely fine electrical properties. However, they all suffer from some disadvantages, chiefly in their mechanical properties. Polystyrene is brittle, while polyisobutylene, although elastic, suffers from cold flow. The use of plastic materials introduces in a more intensified form the problems of ionisation, etc. Nevertheless, these materials are already extensively employed as accessories in power cables. Polystyrene, in particular, is used in cable joints for barriers, as terminations, and so on. While the progress of substitution in this field of activity is necessarily slow owing to the arduous conditions to be fulfilled, yet the trend is quite clearly defined.

Although the chief effort has been to produce a new type, the wholly synthetic-insulated power cable, there has been a considerable amount of work in modifying the existing forms. Many synthetic materials are available as sheets and tapes, generally transparent and colourless, and possessing good electrical characteristics. Cellulose derivatives and notably ethyl cellulose, have been the subject of much work in this direction. But many other very different synthetic materials have received attention, such as polythene, polyvinyl formal, rubber hydrochloride, etc.

Although the elimination of the lead sheath would have much to commend it, no great success has yet been met by the many efforts directed at substitution by synthetic materials. Among materials which have been considered are polyacrylic esters and polyvinyl chloride.

High Frequency. In many respects the field of high frequency and ultra-high frequency may be regarded as new, and consequently represent more a case of innovation rather than substitution. In the sense that coaxial cables tend to replace the conventional type of paper insulated cables, substitution has occurred. This is particularly the case in the branch of high frequency communication. The desirable features are to have a dielectric with as low a dielectric constant and as low a power loss as possible. Although air is unapproached as the best medium, yet the mechanical requirements and practical considerations involve the use of other dielectrics.

In general the polymerised hydrocarbons, polystyrene, polythene, and polyisobutylene, are the most widely employed, and there is already a tendency to refer to these as the high-frequency dielectrics. Where conditions permit, every feasible device has been employed to ensure as much air present as possible, utilising the synthetic material so as to give the requisite mechanical stability. Thus polystyrene has been used in the form of small moulded spacers, as moulded beads, as tape, as thread, and so on. By virtue of their excellent electrical properties these hydrocarbon plastics, and compositions based on them, are also successfully employed, as homogeneous insulations. In these instances the material is simply extruded directly over the central conducting wire. The mechanical properties are then sufficiently good for the remaining processes, e.g. screening, etc., to be carried out without difficulty.

Medium and Low Voltage. The most spectacular examples of substitution have occurred in the very wide field of insulation where rubber has hitherto reigned unchallenged. Although shortage of rubber has necessarily had an accelerating effect on the use of substitutes, yet quite a number had already made much headway in the realm of medium and low voltage cables.

REFERENCES

1 Barron. G.E.C. Journal, 1942, **11**, 70.
2 Du Pont de Nemours and Carbide and Carbon Union.
3 Fawcett. B.P. 336,324; B.P. 350,513.
4 Fawcett. Trans. Faraday Soc., 1936, **32**, 119.
5 Fawcett, Paton, Gibson, Perrin, Williams, and I.C.I., Ltd. B.P. 471, 590/1937.
6 Massey. Trans. Inst. Rubber Ind., 1941, **17**, 325.
7 Richards. British Plastics 1945, 17, 146.
8 Williams and I.C.I., Ltd. B.P. 514,687/1939; B.P. 472,051/1937; B.P. 474,426/1938; B.P. 481,515/1938; B.P. 499,333/1938; B.P. 505,761 1939.
9 Photographs by courtesy of Imperial Chemical Industries (Plastics), Ltd.

CHAPTER XX

POLYSTYRENE

By virtue of the enormous scale of production of polystyrene, e.g. in the United States, and the consequent low cost, it seems likely to play a leading part in the plastics industry in the future. Furthermore, it has the very low specific gravity of 1·05 which adds to its advantage. It will also undoubtedly play a very great role in the electrical field and in modern science. Many production problems have been solved. Objectionable impurities have been removed. Suitable techniques are available to handle the material. The field of use becomes ever wider as the price becomes lower.

In the United States[30] 725,000 tons Buna-S were produced in 1945. This involved something like 200,000 tons of styrene per annum. The fact of having large amounts of styrene available at low cost must have tremendous repercussions upon the use of styrene in other industries, notably in the plastics industry and in the electrical industry.

Production of polystyrene in 1943 in the U.S. was 4 million pounds. In 1945 it was 15 million pounds. By 1948 it exceeded 150 million pounds.

According to Wakeman and Weil:[31]

"With the current development of synthetic rubber, styrene as one of the components of Buna-S, will become a large-tonnage chemical, a fact which will be reflected in increased production of polystyrene plastics in moulded, extruded and film form. In Germany it is to-day one of the most available plastics and is utilised for many applications where cellulose acetate is used in the United States. It has been freely predicted that because of the increased production of styrene caused by the rubber industry, polystyrene will be one of the most available and least expensive plastics in this country after the present war."

Background of Polystyrene. It is actually one of the oldest plastics materials, although there was a long gap between the time when it was first discovered, and its first commercial application. Bonastre[6] obtained styrene in 1831 by distilling *storax*, a resin obtained from a tree. Simon[24] was the first to polymerise styrene. In 1839 he found sunlight caused it to polymerise. He considered the action to be one of oxidation. Styrene was converted into polystyrene in 1845 by Blythe and Hoffman;[5] they heated styrene in a water bath for three days, when it formed polystyrene. They found it took only half an hour at 200°C.

The first synthetic method for making styrene was discovered by

Berthelot[3] in 1869, based on ethylbenzene. This is still the chief principle used in most methods for making styrene. In 1900 Kronstein[12] indicated the possibility of polystyrene as a substitute for glass. He also suggested the use of polystyrene as an ingredient for paints, varnishes and lacquers. He had heated styrene in a sealed tube and noted the successive stages of polymerisation.

The first commercial impetus for the use of polystyrene came from Matthews[16] in 1911, who took out two patents on the subject. He suggested that polystyrene could be used for the manufacture of articles replacing celluloid, ebonite, wood, glass, and so on. However, further development was retarded until comparatively recently owing to the difficulties associated with the material. Apart from being expensive, there were technical difficulties, notably the fact that the material crazed on standing, and spoiled all articles made from it.

Further advances became possible after 1922, when Dufraisse and Moureu[9] discovered protective agents for styrene, which retarded its polymerisation, and facilitated its transport. Typical materials which inhibit polymerisation include hydroquinone, guaiacol, methylaniline derivatives, etc.

Until about 1937 the Germans made a speciality of the material, and little was made elsewhere. Thereafter, production started in Britain, and in the United States. While no great progress has taken place here, the progress in America has been phenomenal, due, let it be said, mainly to the synthetic rubber requirements.

A similar product—Buna S—has likewise been responsible for large scale expansion in German production of polystyrene. In fact the use of polystyrene as a general plastic had reached its most advanced stage in Germany, where it was the leading thermoplastic moulding material.

Properties of Styrene. Styrene is a colourless water-white liquid having a characteristic odour. It boils at 144°C., and the specific gravity at 20°C., is 0·905. In the normal way it has a certain amount of stabiliser present, whose function it is to inhibit polymerisation. Styrene polymerises with great ease under the influence of light or heat or oxygen. Styrene polymerises to give solid products of high molecular weight, which are soluble in aromatic solvents. A great deal of work has been carried out on polymerisation of styrene. In fact, much of the knowledge of polymerisation at the present time has been gained in this field. In particular it has been the chief material used to try out Staudinger's theory of long chain polymers.

A great deal of the early work was carried out by Ostromislensky.[20] The chief point studied was the fact that styrene polymerises in a different manner under different conditions. Thus polymerisation carried out at low temperatures gives vastly different results from polymerisation carried out at high temperatures. Ostromislensky called the material obtained at low temperature α-meta-styrene; that he obtained at high temperature he called β-meta-styrene; yet another type γ-meta-styrene was obtained by the use of catalysts. He suggested that only polymers obtained at temperatures at less than 180° C. were suitable for practical application.

According to Staudinger,[27] polymers prepared at ordinary temperature are tougher and have higher softening point than those produced at higher temperatures. In recent years very much improved polymerisation products have been obtained. The general characteristics of the materials have improved beyond all conception.

Production of Styrene. There has been considerable attention given to methods of producing styrene, although processes are limited to modifications of the first successful methods. In the classical researches of Bertholot on pyrolysis, styrene was made by the thermal decomposition of ethylbenzene. Bertholot also made small amounts from a mixture of ethylene and benzene vapour by pyrolysis.

Styrene occurs in small amounts in many cracked hydrocarbon products, in xylene, in brown coal-tars, and in the products from the cracking of gaseous paraffins. The greatest amount is derived from ethylbenzene, two methods of conversion suggesting themselves being the vapour phase dehydrogenation to yield styrene and hydrogen, while the second is to chlorinate ethylbenzene to yield the alpha- and beta-chlorinated products and then to remove the elements of hydrogen chloride from these bodies. In the dehydrogenation process temperatures of 600°–700° C., were common, the efficiency being only 30 per cent unless dehydrogenation catalysts are used.

It is prepared by the process first discovered by Berthelot, namely the cracking of ethylbenzene. He also prepared it by subjecting a mixture of ethylene and benzene to pyrolysis. Ethylbenzene is obtained in small quantities as a by-product from petroleum refining, and this source is being exploited in the United States. Birch and Hague[4] have found that pyrolysis of gas rich in propane gave appreciable quantities of styrene, e.g. 5 million cubic feet of such gas gave 59,000 litres benzene and 3,400 litres styrene.

The use of ethylbenzene overshadows all other procedures. It is generally prepared by direct synthesis from benzene and ethyl chloride. Under the action of aluminium chloride as catalyst, benzene and ethylene also combine to form ethyl benzene. This is catalytically dehydrogenated or cracked at high temperature, from 800°–950° C. According to one process, when carried out between 500°–600° C., over a suitable catalyst, a yield of 35 per cent is obtained.

Benzene is, of course, obtained by distillation of coal-tar, while ethyl chloride may be prepared via alcohol, or by the direct catalytic interaction of ethylene and hydrogen chloride.

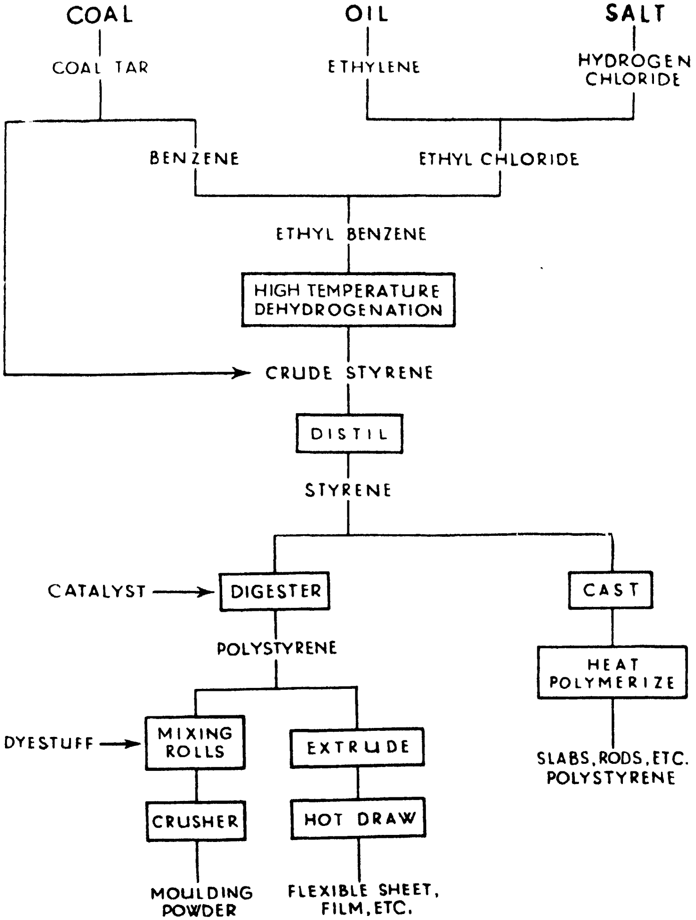


Fig. 168. Flow sheet for polystyrene

One process employed in styrene manufacture involves high temperature treatment of chlorinated ethylbenzene; hydrochloric acid is a by-product of the reaction. A recent modification by Smith[25] starts from ethylbenzene itself which is pyrolysed with a chlorine-supplying agent (carbon tetrachloride) and an acid-absorbent (pyridine or other base). Several advantages result from this procedure: acid formation is largely suppressed and the percentage of styrene in the cracked product is increased. 50 parts ethyl-benzene, 50 parts benzene, 30 parts carbon tetra-chloride and 40 parts pyridine were passed through an electrically heated iron tube kept at 670°C. Carbon tetrachloride produces chlorine at the cracking temperature which combines with the ethylbenzene. Immediate decomposition of the chloroethylbenzene takes place with formation of styrene and hydrochloric acid, the latter being taken up by the pyridine. The above run gave a productivity of 50·4 (productivity being defined as the ratio of ethylbenzene sent through the tube to the styrene produced). When ethyl-benzene alone is run through the tube at 675°C., the productivity amounts to only 18·2. Cracked mixtures obtained by the new technique are well adapted to polymerisation treatment.

Dow[8] has made an interesting comparison of existing methods of production of styrene, illustrating the advantages of the processes used by his Company. He stated that in one method benzene and 95 per cent alcohol were the starting materials being reacted at temperatures of about 285°C., and pressures of 250 lb. per sq. inch over a phosphoric acid catalyst. In another method ethylene is used instead of alcohol. In both these cases very pure benzene is required. The benzene and ethylene must be recycled several times.

The Dow process can use impure ethylene containing as little as 38 per cent of ethylene. Their operating temperature is only 86°C. at the low pressure of 15 lb. per sq. inch. The catalyst is aluminium chloride, giving a yield of up to 100 lb. of ethyl benzene per lb. of catalyst. A much lower grade of benzene could be used in this case. The reaction is carried out continuously, and give almost theoretical yields of ethylbenzene. They can also recover about 80 per cent of the spent aluminium chloride catalyst.

In the American styrene programme, the dehydrogenation of ethylbenzene appears to dominate all other processes, with ethylene from alcohol coming into prominence as a raw material for ethylbenzene. An example of the scale of production is shown by the fact that four companies have contracted to supply styrene monomer approximately as follows:[30]

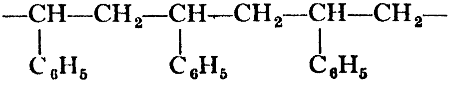
Carbide and Carbon	25,000 tons per year
Dow Chemical Co.	91,200 ,, ,,
Koppers Chemical	37,500 ,, ,,
Monsanto Chemical Co.	30,000 ,, ,,

Styrene polymerises with great ease. The rate of polymerisation is accelerated by heat, by exposure to sunlight or ultra-violet light. Styrene polymerises readily with catalysts. On exposure to sunlight and air, peroxides are formed which act as catalysts for low temperature polymerisation of styrene. It is therefore necessary to have agents present in styrene which will prevent this action . Otherwise it becomes impossible to store styrene for any length of time. Typical inhibiting agents are hydroquinone, guaiacal and derivatives of methyl aniline.

Fig. 169. Storage tanks for styrene

It is possible to obtain a range of polymers with varying molecular weights which may be as high as a million. In general, slow polymerisation at moderate temperatures tends to yield polymers of high molecular weight. Solutions of these show very high viscosity. Rapid polymerisation processes using catalysts and high temperatures usually result in products of low molecular weight. Solutions of these are found to have low viscosity. Low polymers tend to be brittle, have low mechanical strength and have inferior heat-resisting characteristics.

According to Staudinger[26] the phenyl residues are attached to every second carbon atom, thus,



$$\begin{array}{llllll} -CH- & CH_2- & CH- & CH_2- & CH- & CH_2- \\ \ \ | & & \ \ | & & \ \ | & \\ C_6H_5 & & C_6H_5 & & C_6H_5 & \end{array}$$

Recent work of Marvel and Moon[14] tends to support this.

The specific gravity and refractive index do not appear to be greatly influenced by change in molecular weight.

Numerous materials have been suggested as catalysts for polymerising styrene. Oxygen is an effective catalyst giving products of high molecular weight. Peroxide and ozonides have been proposed for the purpose. The use of ozone was suggested by Lawson.[13]

Benzoyl peroxide was suggested by the I.G.[10]

Numerous other reagents have been suggested including concentrated sulphuric acid, stannic chloride, boron tri-fluoride, aluminium fluoride, sodium antimony chloride.

Polymerisation in Emulsion. This is the modern trend of polymerisation. Styrene is emulsified with water with an emulsifying agent and a catalyst and then warmed. The product is pure and light coloured. The emulsion can be made up by shaking styrene with water containing a little ammonium oleate and heating for 24 hours and 140°C. under pressure to form a latex. Copolymerisation may be carried out with reactants emulsified, e.g. 2 parts butadiene or isoprene with 1 part styrene, emulsified with sodium stearate maintained at 60°C. for several days, yield a latex which can be coagulated, milled with carbon black, and vulcanised to give a pliable rubber. Copolymerising with a little divinyl benzene gives a tough infusible insoluble resin, i.e. cross-linking of polymer takes place.

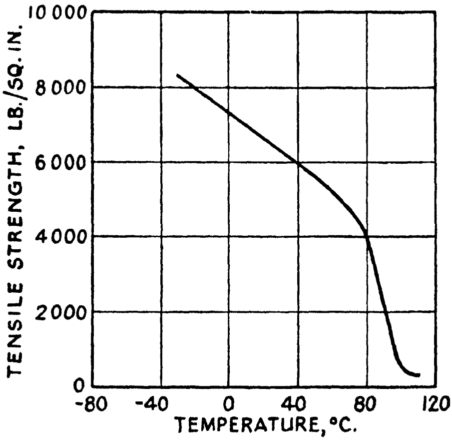


Fig. 170. Tensile strength of polystyrene

The methods used in Germany are typified by the processes used at Schkopau.[34] Two types of very high molecular weight polystyrene were made at Schkopau in the following manner. Hydrogen peroxide was used where an electrical grade polymer was required, otherwise the catalyst used was potassium persulphate. The latter was more active, but the hydrogen peroxide was more easily washed from the polymer.

The formula used was:

Styrene	50 parts
Pure water	50 parts

Potassium persulphate . .	0·1 per cent (based on styrene)
Emulsifying agent . . .	1·0 per cent (based on styrene)

For the emulsifying agent the sodium salts of synthetic fatty acids were generally used, but sometimes Mersolat (sodium alkyl sulphonates) or Mersopan, a mixture of Mersolate and soap, were used. The water and emulsifier were fed into a kettle made from V24 steel or nickel-clad steel. The styrene and finally the catalyst were added, and the temperature increased to 75° C. Complete polymerisation took 7 hours.

Coagulation. Steam was then introduced to strip off 1 to 2 per cent of unchanged monomer, after which the emulsion was pumped to a second kettle, where 1·5 per cent of formic acid (based on the polystyrene) was added, with stirring, to coagulate the polymer. The suspension was filtered on a continuous filter, the powder being continuously washed with pure water, the material then passing along a belt to an Aeroform press, where it was compressed to triangular pieces approximately $\frac{3}{8}$ by $\frac{3}{8}$ by 1 in. This Aeroform press was a polished drum of about 30 in. diameter, with polished-cut triangular grooves of the above dimensions. The roll was heated to 75° C.

The damp powder was fed to the roll and compacted with two polished rolls of about 10 in. diameter. From these, hard, dense pellets were formed. The pellets when dry were ground to a fine powder and packed in 50-lb. paper containers for transport. No stabiliser, plasticisers, colours, or other materials were added.

The Characteristics of Polystyrene. Polystyrene has a number of outstanding properties which have led to a very wide commercial application. In the first place it is far and away the most outstanding plastic material so far as electrical characteristics are concerned. It has outstanding stability in the ordinary temperature range of use. The distortion temperature under load is about 70° C. In this respect it is superior to many other plastic materials. Its promise as a commercial plastic is further enhanced by the low specific gravity 1·05, which gives a pronounced price advantage over many other materials.

It has high tensile strength. Apart from this, it has very high modulus and elasticity, and extremely good dimensional stability under many conditions of temperature, humidity, and stresses. It burns, but quite slowly. If polystyrene is heat softened and stretched it acquires flexibility in the direction of stretch. Orientation of the molecules appears to have occurred. In the drawn form it acquires flexibility, elastic characteristics, and very marked toughness. These properties are not present in ordinary moulded polystyrene. In this condition polystyrene is comparatively brittle, and this is the outstanding disadvantage of the material. Nevertheless, it is far superior to ceramic materials in this respect.

Polystyrene is completely transparent and water-white, having the very high light transmission of about 90 per cent. The refractive index is high at 1·59. These characteristics are of great promise in the field of optical applications, and indeed it is finding use for lenses, dials, etc. It also has the property of transmitting light through rods or sheets, being able to pass light round curves and bends. This property is applied in the illumination of instruments of many types.

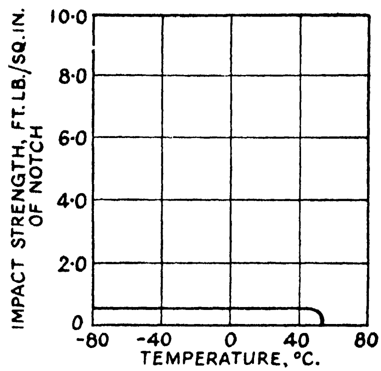


Fig. 171.
Impact strength of polystyrene

TABLE 115

MECHANICAL PROPERTIES OF POLYSTYRENE

Specific gravity	1·05
Tensile strength, lb./sq. in.	6,000–7,000
Modulus of elasticity, lb./sq. in. × 10^5	5·5
Impact strength, Izod, lb. per inch of notch	0·2–0·3
Brinell hardness, 25 kg. load	—
Compression strength, lb./sq. in.	15,000
Shrinkage, inches per inch	0·0001
Mould shrinkage	0·002–0·007 inches per inch

Electrical Properties. Polystyrene has the best electrical characteristics of any organic material. It is far the most outstanding type among plastics in this respect. This is, of course, largely due to the fact that polystyrene is based on a pure hydrocarbon, and therefore has no polar groupings attached. Every desirable electrical characteristic is uniformly good. The excellence of the electrical behaviour is maintained over a very wide temperature range. In particular such features as power factor, dielectric constant, etc., are maintained at low values even at high temperature which is quite exceptional.

The outstanding features of polystyrene are the exceptionally good electrical properties. These are far superior to any other commercial plastic, slightly better even than polythene.

In thin films, the breakdown strength is extraordinarily high, outstanding many plastics, being of the order of 5,000 volts per mil. The power losses are extremely low, power factor being of the order of ·0002 even at very high frequencies. By virtue of its lack of attraction for moisture, it has extremely high resistance to arcing and tracking. The fact that polystyrene does not take up any water is of great value from the electrical point of view. The dielectric constant is also extremely low, and does not vary greatly with frequency. By virtue of these characteristics it is suitable for application at high voltages and at high frequencies.

The ideal high-frequency insulating material has been described as having the following properties:

1. Low dielectric constant.
2. Low power factor.
3. No change in dielectric constant or power factor from very low to very high temperatures.
4. No change in dielectric constant or power factor from low to very high frequencies.
5. Zero water absorption.
6. Very high voltage breakdown.
7. A material non-tracking on puncture.
8. Dimensional stability.
9. Freedom from "creep."
10. Ease of bending, punching, moulding and machining.
11. Mechanical properties sufficient to withstand a designated load under shock or vibration.
12. Availability in sufficient quantity, with a uniform quality at a reasonable price.

Polystyrene is almost perfect. Its main defect is the relative brittleness. There is one other defect, namely, that it cannot be used at temperatures much above 80° C.

TABLE 116

ELECTRICAL PROPERTIES

Volume resistivity, ohms/cms.^{3}	$>10^{17}$
Surface resistivity, ohms/cm.	$>10^{16}$
Breakdown voltage, volts/mil., 0·005 in. thick	4,000
0·125 in. thick	500
Dielectric constant, 50 cycles	2·5–2·6
10^6 cycles	2·5–2·6
Power factor, 50 cycles	0·0001–0·0002
10^3 cycles	0·0002
10^6 cycles	0·0002–0·0003
10^9 cycles	0·0004

The surface resistivity of polystyrene is exceptionally high. The surface resistivity is of the order of 10^{16}, and the volume resistivity is 10^{17} ohms per c.c.

Power Factor. The power losses when polystyrene is used as insulation are extremely low. As a consequence polystyrene has great application in high frequency systems. Even in ultra high frequencies almost into the visible spectrum the loss remains virtually the same. Even at wave-lengths of 10 to 150 centimetres the power factor is still only 0·0004. This is coupled with a dielectric constant which at 2·55 at a frequency of 50 cycles is low to start with. However, this is very little affected by the frequency, and even at ultra high frequency there is little increase.

Matheson and Goggin[15] have shown how the power factor and dielectric constant are relatively little affected by increase in temperature.

TABLE 117

INFLUENCE OF TEMPERATURE ON POLYSTYRENE

Temperature° C.	Power Factor	Dielectric Constant
30	0·00035	2·55
60	0·00044	2·57
90	0·0009	2·60

The manner in which polystyrene retains its electrical characteristics in the whole frequency range has been explained by Morgan,[18]

TABLE 118

INFLUENCE OF FREQUENCY ON POLYSTYRENE

Frequency	Power Factor, %	Dielectric Constant
60 cycles	0·0002	2·60
10^3 ,,	0·00015	2·57
10^5 ,,	0·00022	2·58
10^6 ,,	0·00016	2·60
10^8 ,,	0·00028	2·60

As might be expected from these characteristics, polystyrene is very widely employed for electrical parts; notably in radio and telephone systems. Many electrical parts are made by injection moulding or compression moulding, and also by fabrication from cast slabs or blocks.

It is used for making coil forms, insulators, socket bases, spacers for coaxial cables, etc. The material can be easily machined.

Polystyrene has been widely used in cable technique, in many instances starting from the monomeric styrene. The general principle is to impregnate paper or fabric or any other part of the cable, and then to polymerise *in situ.* The principle involved here has been employed to make seals and blocks in cable joints.[23] It is also used along these lines for the impregnation of coils and condensers. It is also applied in the production of scientific instruments and for display purposes in illuminated signs.

There can be no doubt that polystyrene is destined to play a very important part in electrical equipment in the future. There are indications that the defect of brittleness may be overcome. The ready availability and probable low price coupled with the properties, are a sure guarantee of the future importance of the material.

The other factor which largely accounts for these outstanding properties is the water resistance of polystyrene. It does not absorb water. There is absolutely no take-up of water by polystyrene over a very long period.

Polystyrene is soluble in many solvents. It is soluble in aromatic hydrocarbons, such as benzene, toluene, xylene, etc., in chlorinated hydrocarbons, in ethyl acetate, butyl acetate, cyclohexanone, and so on. It is not affected by water, acetone, alcohol, by glycerine, or glycols. It withstands all alcohols, concentrated acids and alkalis. It will even resist attack by hydrofluoric acid and bromine. This resistance to chemical corrosion gives it a wide field of application for containers and packages associated with many cables. It is also resistant to fats and greases, and consequently finds application for foodstuff containers, particularly as mouldings for refrigerators. It tends to discolour after long exposure to sunlight or ultra-violet light.

The cold flow, or gradual distortion under heavy load, is very low at room temperature and does not become at all evident until about 70° C. is reached. The dimensional stability of polystyrene at ordinary temperatures is exceptionally good. It is also interesting to note that samples cooled in solid carbon dioxide have about the same impact strength as at room temperature. (In actual tests, notched Izod compression moulded test bars were placed on a block of solid carbon dioxide for 2 hours and then broken in the normal way; an average value of about 0·275 foot-pound of energy to break was obtained. Injection moulded test bars under similar conditions gave an average impact value of 0·4 foot-pound energy to break.) The thermal softening point is about 80° C. This is the point at which distortion under moderate load first reaches a small specified value.

Apart from its tendency to be brittle, polystyrene has also the disadvantages of tending to craze on standing. This has been attributed to impurities such as ethylbenzene, etc., remaining in the styrene. Latterly, as the quality of polystyrene has improved, there has been a diminution in this characteristic. However, it is still a fact that there appear to be internal stresses left in the products moulded from polystyrene which ultimately result in crazing. This is eliminated by normalising the materials, and quite large quantities of normalised polystyrene are produced at the present time.

TABLE 119

ACTION OF CHEMICAL REAGENTS ON POLYSTYRENE

24 HOURS AT 20° C.

	% Change in Weight
Hydrochloric acid (conc.)	+0·07
Hydrochloric acid (15%)	—
Nitric acid (conc.)	+0·52
Nitric acid (15%)	+0·5
Sulphuric acid (conc.)	—
Sulphuric acid (15%)	—
Sodium hydroxide (5%)	—
Sodium hydroxide (20%)	—
Glacial acetic acid	+0·65
Acetic acid (15%)	+0·05
Calcium chloride (10%)	—
Saturated bromine water	+2·00
Saturated chlorine water	+0·50
Water	—
Carbon tetrachloride	Soluble
Tetrachlor ethylene	Soluble
Ethylene dichloride	Soluble
Benzene	Soluble
Ether	Soluble
Toluene	Soluble
Ethyl acetate	Soluble
Amyl acetate	Soluble
Acetone	Soluble
Naphtha	+0·7
Kerosene	+0·4
Ethyl alcohol	+0·1
Glycerine	—

Cast Polystyrene. The ready availability of monomeric styrene has led to the use of the material in this form, which is very convenient. A great deal of work is now carried out whereby styrene is polymerised *in situ.* Many articles are made by casting styrene, i.e. pouring the styrene into a mould and causing it to polymerise by heat, oxygen, the use of catalysts, etc. Apart from the direct casting of articles, many products are made which are impregnated or encased in polystyrene, either to enhance their electrical characteristics or to provide protection against humidity, etc. Much work has been done in the preparation of cable joints.[21] The factors which have to be considered in carrying out such work include:

(*a*) Heat of polymerisation.
(*b*) Temperature employed.
(*c*) Shrinkage of the material due to polymerisation.
(*d*) Formation of bubbles.

High heat of polymerisation is involved, and this has a limiting influence on the thickness of the product. Polymerisation is slow at temperature below 100°C. On the other hand styrene tends to volatilise fairly easily above this temperature. During polymerisation there is a shrinkage of about 15 per cent accompanied by increase in density. This must be taken into consideration. In the presence of oxygen a certain amount of discoloration may occur.

Cast slabs of polystyrene may be machined without difficulty in the preparation of numerous articles. Many electrical parts are made in this manner by fabrication from slabs or blocks of cast polystyrene.

For working and fabricating polystyrene, the following procedure has been recommended for "*Distrene*",[7]

> Speeds of approximately 1,000 r.p.m. with a light cut are necessary for turning operations. It is essential to keep the material cool, and soluble oil lubricant is recommended.

When drilling, a speed of approximately 300 r.p.m. is desirable. Soluble oil should be freely used with frequent clearance of drill.

Polystyrene can be milled on standard horizontal or vertical milling machines; again soluble oil lubricant should be freely used.

Sheets may be sawn without difficulty although the material must be well lubricated to obviate heating up. Saw speeds of 3,500 r.p.m. has been found well suited to the material.

Moulding of Polystyrene. The evolution of polystyrene as a major moulding plastic, has hinged upon its suitability for use by injection moulding. Full advantage of its admirable properties, high electrical performance, small water absorption, transparency, etc., could not be taken while the ordinary compression method of moulding was the sole procedure available. For compression moulding, temperatures between 120°C. to 180°C. may be used with pressures between ¼ to 1 ton per sq. inch, depending on the type of product being made.

A leading reason for the expanding application of polystyrene is the fact that it is one of the most suitable materials for use by injection moulding. For this, it requires no modification with plasticisers, but as powdered polystyrene it is adequate for feeding into almost any injection moulding machine. Once taken above the softening temperature, it flows very readily, and in the temperature range employed for injection moulding it behaves almost like a fluid. The temperatures may vary between 190°C. to 220°C. while injection pressures range from 2 tons up to 15 tons per sq. inch. The flow characteristics are excellent, and well suited to the technique. It chills very rapidly, shows no inclination to stick to mould surfaces, and can be released quite easily. It acquires high polish and lustre from the surface of the mould, and retains the excellent transparency which is such an attractive feature. The flow is so good that very thin sections may be filled without any difficulty. By virtue of its transparency the colour possibilities are unlimited, and it is available in many shades.

Flow Characteristics of Polystyrene for Moulding. Under changes of temperature, polystyrene undergoes many interesting changes of condition. The flow characteristics are most varied. At room temperature it is a hard rigid solid. When heated it first changes to a rubbery material which has almost pronounced elasticity, comparable with that of rubber. It then becomes fluid, the viscosity decreasing as the temperature rises.

The rubber-like behaviour of polystyrene when warm has roused the greatest interest. It has been studied by many workers. The outstanding work was carried out by Whitby.[33] Polystyrene made by polymerisation at low temperature begins to show rubber-like elasticity at 65°C.

The following experiment shows how rubbery the material becomes. A strip of polystyrene was heated to 95°C., stretched to an elongation of 450 per cent and immediately released. The strip contracted at once to an extension of only 50 per cent and after 200 seconds it had returned to its original length. When held in the extended form for 10 minutes, the extension immediately after release was 175 per cent and after 200 seconds it was 75 per cent. This illustrates clearly the limited flow properties of the resin at 95°C.

With rise in temperature above this, the properties of a true fluid became more pronounced and the elastic properties slowly disappeared.

Stretching during the rubbery stage profoundly modifies the strength characteristics, and, therefore, it must be given careful consideration during all stages of any forming process. Strength is increased when the tensile forces are parallel to the direction of flow, and reduced when in the direction at right angles to it.

Weith[32] examined the behaviour of polystyrene granules when heated from 95°C. up to 225°C. His idea was to see how polystyrene behaved in the temperature range of injection moulding. The lower temperature is where polystyrene shows very strong elastic behaviour. The polystyrene was heated under controlled conditions for one hour and the resulting mass examined.

"The product by carrying out the above procedure at 135°C. looked somewhat like a loosely packed snowball with a thin coating of ice over its surface. The individual granules were clearly visible and appeared to be simply fused together at the points of contact as they existed in the original loosely packed granular material. Obviously there was little real liquid flow. Increasing the temperature to 165°C. produced definite changes in appearance, although the opaque white character of the snowball was still retained. Some of the spaces between the particles assumed the shape of bubbles, indicating that the particles fused enough to form continuous walls around what were formerly the spaces between discrete particles, and the glassy or icy appearance at the surface appeared to go deeper into the mass. At 185°C. the fusion was practically complete, but the viscosity was so high that bubbles were trapped in the mass and gave it a white translucent appearance.

"The products obtained at 210°C. and 225°C. present a different appearance from those just described. Complete fusion has finally been obtained, and most of the bubbles or voids are eliminated, leaving the material with a clear, transparent, glass-like form. Even at these temperatures, however, the viscosity was found to be high, and the molten resin could not be poured out of the flask. The rate of flow was so slow that the mass cooled before it moved more than a fraction of the way down the side of the container."

The behaviour of the resin between 185° and 225°C. is of particular interest, because, as already pointed out, this region is in the operating range of most commercial injection moulding equipment. For best results in moulding it is necessary that the material be fairly fluid at the moulding temperature so that the pressure applied will be transmitted throughout and will force the resin into all parts of the mould. On the other hand, if the viscosity is too low, the plastic will flow out through the cracks between different sections of the mould and will cause what is known as flash. This flash makes necessary an expensive finishing operation on the moulded piece. A third and most important consideration in the economics of injection moulding is the time cycle required for the complete moulding operation. Obviously this is a function of the time required to cool the resin to a state such that it can be discharged from the mould without deforming.

This description of the flow characteristics at various temperatures illustrated that polystyrene is exceptionally well suited to the process of injection moulding. It has the characteristics necessary for production of clean, sharply defined mouldings at maximum speed. The increasing application of polystyrene by injection moulding is practical confirmation of these views.

Polystyrene may be extruded as rods and tubes. However, greater care is necessary than when other plastics are extruded. Bailey[2] has given an excellent account of the factors which must be considered.

Generally speaking, when extruded, polystyrene must be more uniformly heated than most other plastics. If this is not done, the extruded piece tends to readjust itself into the shape of the original grains, and the surface becomes lumpy and rough. Attempts to obviate this trouble by going to higher temperatures and using an extensive system of breaker plates is only partially successful owing to the poor heat conductivity of the material, and in many cases a higher temperature is not permissible.

With rods of heavy section, the matter of cooling must be considered. Most polystyrene tends to develop bubbles when extruded into the atmosphere, and this is particularly troublesome when making heavy sections. These bubbles, however, can be suppressed by applying outside hydrostatic pressure to the plastic. Similar methods are used to prevent the formation of voids in other materials, e.g. polythene.

While cellulose acetate and methyl methacrylate can be extruded with a glass-like surface, polystyrene is best handled at temperatures which give a frosted or matt finish. In some cases, polished rod is wanted which requires the removal of this frosted layer, hence rods are made from 0·005 in. oversize for small diameters to 0·015 in. oversize in large diameters to permit finishing to exact size.

The Use of Plasticisers. Polystyrene can be modified by the use of plasticisers, such as tricresyl phosphate, dibutyl phthalate. In most cases, however, the advantages derived are of less value and are outweighed by the disadvantages. In general, plasticisers lower the softening point of polystyrene, which is clearly undesirable. Also, every ordinary plasticiser has an adverse influence on the electrical characteristics, which is serious enough to detract from the electrical applications. They also raise the water absorption considerably.

As a consequence, until comparatively recently, polystyrene has not found many applications in the plasticised form. There have been a few exceptions. The most effective plasticiser to date has been chlorinated diphenyl. Suitable grades raise the softening point of the position by as much as 10° C., and furthermore make the product non-inflammable—a valuable advantage. The electrical characteristics are not unduly affected.

Substituted styrenes, sometimes polymerised, have also been used as plasticisers. Thus, polymerised α-methyl-styrene can be used even up to proportions of 70 per cent of the total mixing. Although the softening temperature is lowered, the electrical properties are excellent. According to New,[19] such materials possess very satisfactory power factors over a wide range of frequencies and temperatures. Thus, a mixture of 40 parts polystyrene and 60 parts of the grade known as *Polymeth* 2 at 110° C. and 50 cycles per second, has a power factor of 0·0007; at room temperature, and 100 megacycles per second, the power factor is 0·0014. Jones and Brown[11] have described a new high temperature-resisting material—polydichlorostyrene—having very interesting characteristics.

TABLE 120

PHYSICAL PROPERTIES OF STYRAMIC (POLYSTYRENE-CHLORINATED DIPHENYL)[28]

	Styramic	A Typical Commercial Grade of Polystyrene
*Specific gravity 25/25° C.	1·358	1·049
*Specific volume, cu. in./lb.	20·45	26·42
**Mould and age shrinkage, 6 months, in./in.	0·0025	0·0024
*Heat distortion temperature	84·5–86° C.	76–78° C.
Flow temperature	138° C.	130° C.
*Water absorption, 24 hours, %	0·046	0·078
Burning rate, in./min.	Chars slightly but will not burn	0·77
*Dielectric constant, 300 kc. dry	2·55	2·60
*Dielectric constant, 300 kc. 96 hours water immersion	2·60	2·60
*Power factor, 300 kc. dry %	0·04	<0·03
*Power factor, 300 kc. % 96 hours water immersion	0·04	<0·03
*Loss factor, 300 kc. dry %	0·1	<0·08
*Loss factor, 300 kc. 96 hours water immersion, %	0·1	<0·08
Machinability	Excellent	Excellent

* Compression moulded. ** Injection moulded.

Polystyrene has been mixed with polyisobutylene to give tough flexible materials retaining all the electrical characteristics.

Copolymers of Styrene. The search for a suitable modified material has been carried on for many years. The greatest success seems to have been attained by the addition of modifying agents actually in the molecule, i.e. by copolymerisation. Styrene lends itself well to copolymerisation processes. It is, of course, part of the copolymer with butadiene, which is Buna S. rubber. In this instance the composition is butadiene 75 parts, styrene 25 parts. When the styrene predominates so that butadiene acts as a modifying agent, very interesting tough flexible materials are obtained. In these high electrical properties are present, while the flexibility and softening point are considerably improved.

A typical material made on this basis is "Styralloy 22," which has high toughness and softening point, retains a flexibility down to −70°C., and is resistant to corrosive discharge at high temperature.

Many other copolymers have been made, for example, with acrylic esters, with methacrylic esters, with butylene, and so on. None of these has as yet attained any great commercial application.

Fillers. While polystyrene has been expensive, and used exclusively for electrical applications, fillers have not been added, owing to the adverse effects on electrical properties. Efforts have been made to utilise fillers such as mica, powdered quartz, and powdered glass, etc. All showed relatively poor high frequency insulating properties. This deterioration was emphasised, after water immersion. Soluble dyestuffs have been used to give various colour effects.

With the expanding application of polystyrene for general moulding purposes, there is bound to be a wider use of filling materials, particularly to obtain a variety of decorative effects. There is no difficulty in mixing fillers by ordinary procedures on hot mixing rolls. An alternative procedure is to add the fillers to monomeric styrene prior to polymerisation.

In the electrical field it has been shown by Scott and New[22] that up to 25 per cent of powdered lead chloride raises the dielectric constant without unduly affecting the power factor.

Applications of Polystyrene. Polystyrene has the ability to retain high impact strength at low temperature. It has therefore been widely applied for refrigerator parts. It is able to withstand the effect of food acids and cleaning agents. It is also unaffected by moisture. As a result it has been used as insulating frames, freezing unit doors, drip trays, and food containers. Unlimited colour possibilities add to the attraction for such uses.

The outstanding chemical resistance, notably the way in which it withstands acids, alkalis, and alcohols, have led to its use for many industrial purposes. It is employed for making accumulators and other electrical equipment of this type. It is used as a container for hydrochloric acid, and also for bottle closures.

The transparency of polystyrene and its light transmitting characteristics have been widely applied. Instrument panels, dials, and lenses, are made from it. It also has the property of edge-lighting which finds application for aircraft instrument illumination and other similar purposes. In this application there is complete elimination of glare.

TABLE 121

INFLUENCE OF FILLERS

Material	Dielectric Constant	Power Factor	
		1 megacycle per sec. (approx.)	40 megacycles per sec. (approx.)
Distrene 60	2·1	0·0002	0·0001
Distrene 80	2·3	0·0002	0·0001
Trolitul	2·3	0·0003	0·0003
20% Mica 80% Distrene 80	2·3	0·0028	0·0002
40% Mica 60% Distrene 80	2·6	0·0097	0·0008
60% Mica 40% Distrene 80	2·9	0·0153	0·0026

60% Mica—40% Distrene 80.

Frequency in Megacycles per sec.	Power Factor
0·1	0·0545
0·2	0·0275
1·1	0·0153
6·4	0·0108
14·8	0·0075
29·3	0·0045
37·6	0·0026

The crystal clarity of the material has led to its use for numerous mass produced lenses for magnifying glasses and a variety of instruments. Polystyrene has already been used for the construction of tiles for internal construction, notably for bathrooms and kitchens, where the dimensional stability, the complete resistance to moisture and the exceptional colour effects have made it extremely attractive.

It seems clear that with the reduction in cost of polystyrene, which is rapidly being realised, there will be a much wider use in a multiplicity of mouldings of every description. It is already widely used for containers and similar applications in Germany where it leads cellulose acetate in volume and diversity of products.

Polystyrene has been employed in the United States for the production of bottles and containers. The process employed is known as extrusion blowing. Plastic polystyrene is extruded as a tube into a mould. Fluid pressure is then exerted, when the tube takes up the shape of the mould. The mould containing the blown shape passes on for cooling, while another takes its place.

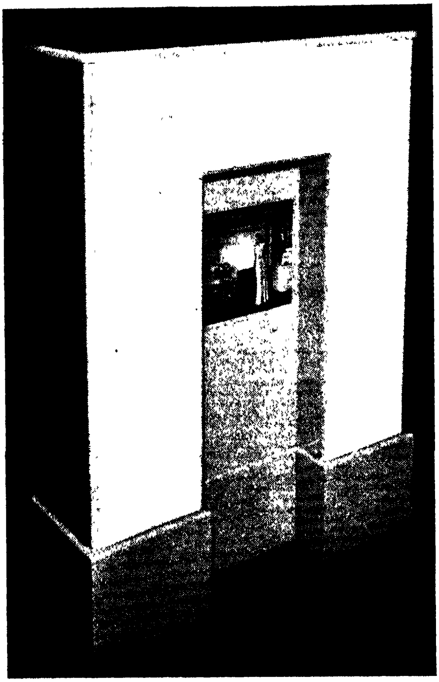


Fig. 172. Tiles moulded in polystyrene

Flexible Forms of Polystyrene. The brittleness of polystyrene prevents its use for many applications. It would be very desirable for electrical uses in the form of films, sheets, and filaments. In the ordinary way these would be far too brittle. Methods have been developed for overcoming this disadvantage. The process involves drawing the polystyrene while it is still hot and plastic. In many respects the proceeding resembles the cold drawing of nylon filaments. One early type of flexible polystyrene is known as "*Styroflex*."[29] In the production of fibres the plastic polystyrene is extruded through an orifice under quite high pressure, 50 to 100 atmospheres. The plastic thread as it emerges from the die is drawn out so that the diameter is greatly reduced. The elongation is increased to about 5 per cent instead of 1 per cent. There appears to be an orientation of polystyrene molecules in the direction of stretch, and this imparts flexibility and strength to the final product. Very fine threads can be produced in this manner. Profiled threads and tubes may also be prepared along similar lines.

The production of flexible polystyrene film presented difficulties. Bailey has described the procedure. Extrusion of sheet through a slit with subsequent drawing was not satisfactory, since all the strength and flexibility was in one direction only—along the length. The problem was solved by extruding a tube which was passed over a stretching frame of greater diameter. In this manner the tube was drawn, and at the same time stretched in the transverse direction, so that orientation of the molecules took place in both directions. The two short sides were then cut out, leaving the two sheets of flexible film. It has become available in continuous rolls in thicknesses up to 0·020 inches. Physically this resembles "Cellophane."

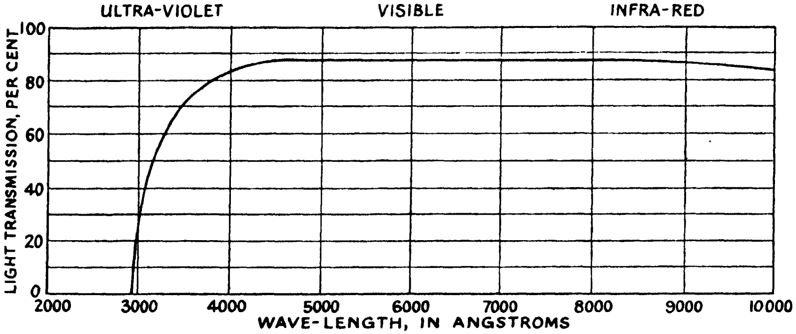


Fig. 173. Light transmission of polystyrene

The flexibility conferred on polystyrene in this manner is retained at low temperatures, but is completely lost if the material is heated. When heated the orientated molecules tend to return to their original condition and the material becomes brittle. The sheet will stretch up to a maximum of about 50 per cent elongation.

The material retains its flexibility at ordinary temperatures indefinitely. Flexible threads and foils of polystyrene have been employed. in the production of coaxial cables. A number of patents have been published involving the use of flexible polystyrene wound spirally as the insulation in such cables. Articles may be stamped out from these sheets and are employed for washers, spacers, etc.

Polystyrene Solutions. A polystyrene cement is available for use in cementing sections, fastening coils to coil forms, or making seals on high frequency electrical equipment. This cement applied in liquid form to the surfaces to be joined, welds smooth surfaces of polystyrene with no loss of electrical characteristics.

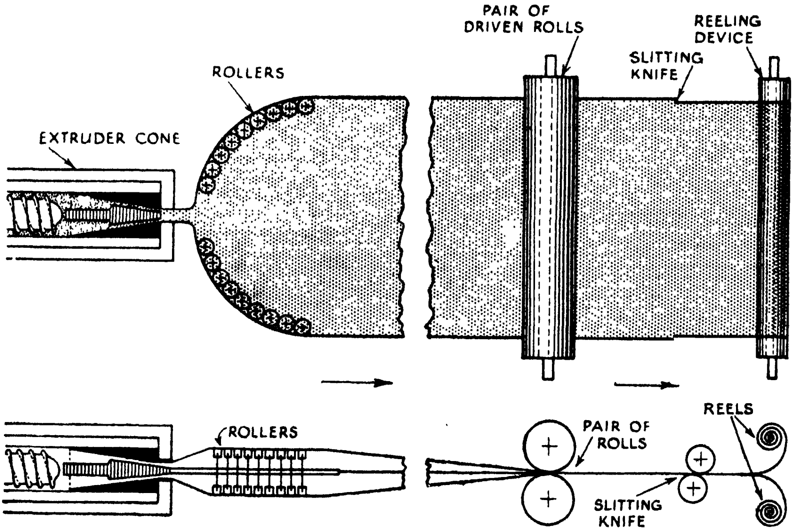


Fig. 174. Production of polystyrene foil

One of the first applications of glass-clear polystyrene was in the form of prisms. A German concern[1] was granted a patent for the manufacture of a glass substitute for lenses by polymerisation of styrene in presence of certain anti-crystallising agents (such as sulphur chloride and chlorinated hydrocarbons). These polystyrene resins were also used as a cementing agent for glass lenses in place of Canada balsam.

Polystyrene in Protective Coatings. The excellent colour and chemical stability of polystyrene resins early led to attempts to use them in protective and decorative coatings. A number of such applications have been made successfully from solutions of high-molecular-weight polystyrene, usually plasticised with one of the chemical plasticisers such as tricresyl phosphate, dibutyl phthalate, or the like. High molecular-weight polystyrene is, however, incompatible with most of the ingredients commonly used in paints and varnishes, particularly the drying oils—a fact which has until recently prevented them from being widely utilised for coating purposes. Recent work upon the control of the styrene reaction has now made practical the production of styrene polymers of relatively low molecular weight which are readily soluble in the drying oils to produce oleoresinous varnishes.

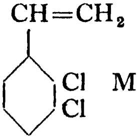
Perhaps the most outstanding feature these new styrene resins impart to oleoresinous varnish films is the combination of excellent flexibility and film strength with high resistance to moisture absorption and moisture permeability. These two properties are seldom found together in resin-oil varnishes, but are necessary for many important applications, including the fabric and paper-coating fields, waterproof sandpaper, varnished cambric and tapes, for electrical insulation, and coatings for metal food-containers, and for improving the moisture resistance of transparent cellulose derivatives used in packaging foods, tobacco and other products.

These new oil-soluble styrene products also retain the desirable properties of good colour, heat stability, and high resistance to alkalis and acids. The extent to which these properties are preserved in the varnish film depends largely upon the ration of resin and drying oil used in preparing the varnish. A varnish containing as much as 50 per cent resin and 50 per cent tung oil for instance, yields a tough, flexible film of outstanding moisture and alkali resistance and of unusually good gloss and levelling properties. Varnishes containing 2 to 4 parts oil to 1 part styrene are still more flexible, though of somewhat lower moisture and chemical resistance, and are well suited for electrical insulating purposes, since they have a high dielectric breakdown of around 2,200 volts per mil.

Polychlorstyrenes. Efforts have been made to improve some of the properties of polystyrene by introducing chlorine into the benzene nucleus of styrene. Michalek[17] was successful in achieving this. The product polydichlorstyrene is marketed as Styramic H.T by the Monsanto Company.

Michalek started with dichlorbenzaldehyde $C_6Cl_2H_3$.CHO, which was treated with methyl magnesium iodide. The product after hydrolysis is dichlorphenyl methyl carbinol $C_6Cl_2H_3$.CH_3.CHOH.

When the elements of water are removed nuclear substituted dichlorstyrenes are obtained. A typical one is 2:3 dichlorstyrene



M.P. 75—78°C.

When 2:3 dichlorstyrene is charged in a closed glass vessel with 0·05 per cent benzoyl peroxide and kept at 70°C. for 48 hours, a clear tough polymer is obtained. This has a density of 1·280 and refractive index 1·5724. It has good resistance to chemicals and withstands boiling water. It has heat distortion temperature about 30°C. higher than ordinary polystyrene. It also resists combustion. The electrical characteristics are of the same high order as polystyrene.

REFERENCES

1 A.E.G. G.P. 600,945/1934.
2 BAILEY. *Modern Plastics*, 1943, December, 90.
3 BERTHELOT. *Bull. Soc. Chem.*, 1936, **6**, 296.
4 BIRCH AND HAGUE. *Ind. Eng. Chem.*, 1940, **32**, 1301.
5 BLYTHE AND HOFFMAN. *Annalen*, 1845, **53**, 314.
6 BONASTRE. *J. de pharmacie*, 1831, **17**, 338
7 Distrene. Trade Mark of B.X. Plastics, Ltd.
8 DOW. *Ind. Eng. Chem.*, 1942, **34**, 1267.
9 DUFRAISSE AND MOUREU. *Comptes rend.*, 1924, **178**, 824.
10 I.G. Farbenindustrie. B.P. 365,217.
11 JONES AND BROWN. *Mod. Plastics*, 1944, August, p. 93.
12 KRONSTEIN. *Berichte*, 1902, **35**, 4153.
13 LAWSON. U.S.P. 1,890,060/1932.
14 MARVEL AND MOON. *J.A.C.S.*, 1930, **52**, 376 et seq.
15 MATHESON AND GOGGIN. *Ind. Eng. Chem.*, 1939, **31**, 335.
16 MATTHEWS. B.P. 16,277/1911.
17 MICHALEK and Mathieson Alkali Co. B.P. 564,828, 1944, 564, 829.
18 MORGAN. *Ind. Eng. Chem.*, 1938, **30**, 273.
19 NEW. B.P. 546,571/1942.
20 OSTROMISLENSKY. *Chem. Ztg.*, 1912, **36**, 199 U.S.P. 1,683,402/1928 et seq.
21 SCOTT. Electrical Communications, 1937, **16**, 51.
22 SCOTT AND NEW. U.S.P. 2279,762/1942.
23 SCOTT AND WEBB. Electrical Communications, 1938, **17**, 88.
24 SIMON. *Annalen*, 1839, **31**, 267.
25 SMITH. U.S.P. 1870,878/1932.
26 STAUDINGER AND STANLEY. *Chem. and Ind.*, 1938, **57**, 93.
27 STAUDINGER AND FROST. *Berichte*, 1935, **68**, 2351.
28 Styramic. Dow Technical Literature.
29 Styroflex. *Kunstoffe*, 1940, **3**, 353; B.P. 452,779.
30 U.S. Styrene Production. Baruch Report, Washington, 1942.
31 WAKEMAN AND WEIL. *Ind. Eng. Chem.*, 1942, **34**, 1387
32 WEITH. *Ind. Eng. Chem.*, 1940, **32**, 1301.
33 WHITBY. *Trans. I.R.I.*, 1930, **5**, 184.
34 C.I.O.S. XXVIII–13, p. 11.

CHAPTER XXI

POLYVINYL CHLORIDE AND DERIVATIVES

POLYVINYL CHLORIDE is one of the most important commercial synthetic materials which is already produced at a rate of many thousands of tons per year. It is commonly known as P.V.C. It is widely used in the United States, in Germany, in Great Britain, and in Russia.

In the U.S. in 1943 output was 83 million pounds. And a number of new plants were building. In 1947 output reached 100 million pounds and in 1948 it was 141 million pounds.

In the summer of 1944 German production was:

Bitterfield	I.G. Plants	1,400 tons per month
Schkopau		600 tons per month
Ludwigshafen		200 tons per month
Wacker		200 tons per month

giving capacity of 28,000 tons per annum.

British production is of the order of 10 million pounds per annum.

There have been extraordinary developments with polyvinyl chloride as a direct consequence of the shortage of rubber during the war. Wire and cable industries in every country have used the material on a large scale. But intensive development work with consequent appreciation of the properties has widened the scope. Many diverse fields have opened up, such as waterproof coatings for fabrics, extruded tubing, moulded articles, fabricated sheets, etc.

The outstanding features of the rubber-like masses which can be produced are:

(*a*) Resistance to prolonged flexing.
(*b*) Resistance to sunlight.
(*c*) The materials do not swell in the presence of oils and solvents.
(*d*) Resistant to corrosion.
(*e*) Resistance to moisture.
(*f*) Resistance to oxidation.

Historical Background. Vinyl chloride was obtained as long ago as 1838 by Regnault,[17] who discovered that it could be obtained by the reaction of dichlorethane with an alcohol solution of caustic potash. He discovered that when this was subjected to the action of sunlight in a sealed glass tube, it polymerised to from a white powder. He also discovered vinylidene chloride. Baumann[3] in 1872 succeeded in polymerising the vinyl halides to white, viscous, plastic masses which were unaffected by solvents or acids.

The real background to the present importance of polyvinyl chloride was supplied by the work of Ostromislensky,[15] whose main objective at the time was to make synthetic rubber. His work is of outstanding importance. As far back as 1912 he outlined the conditions for the polymerisation of vinyl chloride, vinyl bromide, and other derivatives.

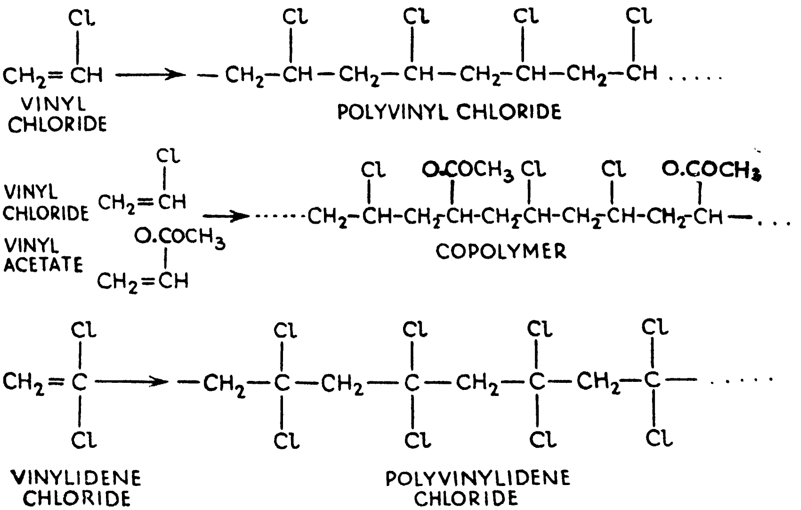


Fig. 175. Polyvinyl chloride and derivatives

He also indicated a method for preparing rubber-like materials from the polymerised products. Ostromislensky was particularly interested in seeking a connection between the polymers of vinyl chloride. He separated fractions from his polymerised vinyl chloride, which he called α, β, γ and δ cuprene chlorides respectively.

He actually found that the composition of a vinyl chloride polymer $C_{32}H_{48}Cl_{16}$ was the same as he obtained for a chlorinated synthetic butadiene rubber, and also it was the same as for the chlorinated isoprene synthetic rubber. The similar solubility behaviour of these materials and their common ability to be transformed into plastic masses suggested to him that vinyl chloride was identical with the chlorination products of butadiene, isoprene, and natural rubber. This work first showed the possibility of the industrial utilisation of the vinyl chloride polymers. Ostromislensky also developed suitable technique for carrying out polymerisation.

Polyvinyl chloride is an odourless, tasteless, non-inflammable white powder, having excellent chemical resistance and very low water absorption.

It is obtained by the polymerisation of vinyl chloride, which is actually a gas at normal temperature, the liquid having a boiling point at −14° C.

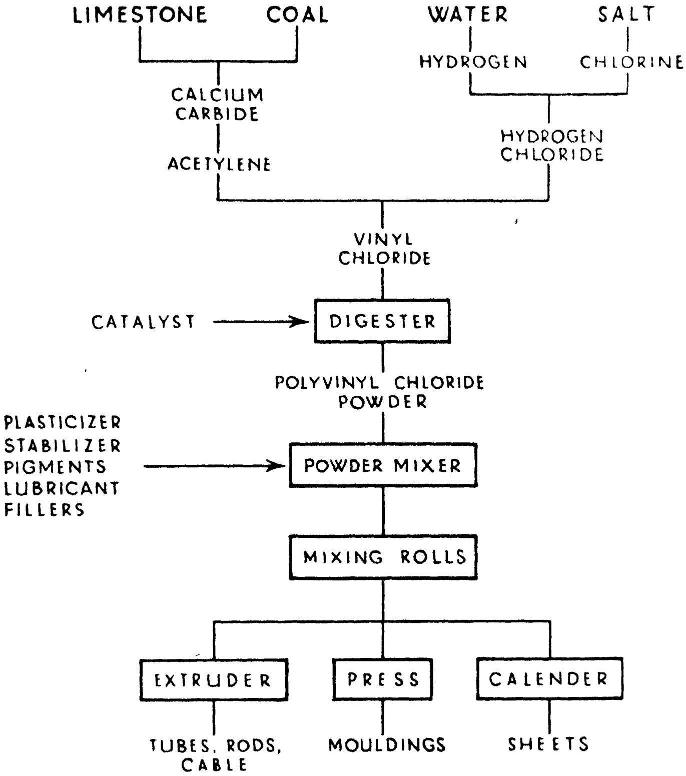


Fig. 176. Flow sheet for polyvinyl chloride

Vinyl chloride is obtained chiefly from acetylene, by passing it with hydrogen chloride over a contact catalyst.

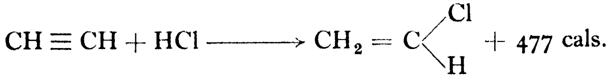
There are a number of methods of production of vinyl chloride based on acetylene, dichlorethane, and so on.

Production of Vinyl Chloride from Acetylene. The process of manufacture of vinyl chloride from acetylene actually consists of effecting the union of hydrogen chloride with acetylene in the presence of a catalyst.

The patent literature relating to synthesising vinyl chloride from acetylene may be summed up in a fundamental formula of passing acetylene and hydrogen chloride, compressing up to 1—1·5 atmospheres, over a contact catalyst. The main points of difference among the many variations of this process is the definition of the temperature range, the selection of catalyst and the plant required for the procedure.

Fig. 177. Polyvinyl chloride polymer, plasticisers, etc., being premixed in a blade mixer prior to the main mixing process[26]

The synthesis of vinyl chloride by this method is carried through according to reaction:



$$CH \equiv CH + HCl \longrightarrow CH_2 = C\begin{matrix} Cl \\ H \end{matrix} + 477 \text{ cals.}$$

Vinyl chloride

The temperature level, with liquid catalysts, in the majority of cases is maintained between 60° C. and 80° C. The hydrochloric acid solutions of metal chlorides are the most popular catalysts used in the process.

The following reagents are recommended for application as dry catalysts: (*a*) mercuric chloride precipitated on silica gel; in this case the process of obtaining vinyl chloride may be performed at reduced temperatures from 20° C. to 30° C. ; (*b*) activated carbon, here the reaction is conducted at higher temperature up to 200° C.

The yield of vinyl chloride on the basis of acetylene is usually of the order of 55–70 per cent, and an additional heat economy in the process can be effected by re-circulating exhaust gases.

Judging by the numerous American patent specifications for deriving vinyl chloride from acetylene, it is evident that this method is definitely favoured in the U.S.A.

It is also worth while noting that the rapidly expanding use of the acetylene process for vinyl chloride synthesis in America coincided with a similar tendency in Germany. In that country the great reactivity of vinyl chloride, yielding derivatives of far-reaching technical and strategic importance, had been assiduously exploited, and manufacture is carried out on a large scale.

Vinyl chloride is a commodity quite amenable to transportation, and may be conveniently carried in steel bottles or in tank cars.

Vinyl chloride can be made by the hydrolysis of dichlorethane. In this process dichlorethane and alcoholic caustic soda are placed in an iron-jacketed vessel and dichlorethane is gradually added with continuous stirring. The temperature is regulated by hot water passing through the jacket. The reaction is completed after four hours at a temperature of about 90°C. The procedure is accelerated by increasing the amount of alcohol. The residue left in the vessel at the end of the process may be used over again. The yield of vinyl chloride by this method is between 75 and 85 per cent.

Another method involves the pyrolytic treatment of dichlorethane in the presence of a suitable catalyst. The dichlorethane in the form of gas at high temperature is passed over the catalyst and is cracked. An excellent yield of vinyl chloride is obtained, for example, by passing the vapours over activated carbon between 240° C. and 350° C. In spite of the advantages this method offers by virtue of the continuity of the process, it is still in the early stages and is being developed.

$$CH_2Cl{-}CH_2Cl \longrightarrow CH_2{=}CHCl + HCl$$

Vinyl chloride polymerises by the action of the usual range of catalytic agents. The process may be carried out in solution or under conditions of emulsion polymerisation. It is promoted either by light or by heat. The former has already been described.

Heat Polymerisation of Vinyl Chloride. Under the influence of heat, vinyl chloride readily polymerises to form resinous substances varying in properties over an extensive range, from rubber-like plastics to hard solids. One method is to add the vinyl chloride together with an acetone solution of the catalyst to alcohol. At 50° C. the reaction may take eighty hours.

Many reagents have been proposed for the use as catalysts in thermal polymerisation of vinyl chloride. It has been suggested, for instance, in Germany,[13] to catalyse the reaction with the aid of salts of uranium, cobalt, and lead.

The Carbide and Carbon Chemical Corporation[7] employed tetraethyl lead. Du Pont de Nemours[9] polymerised vinyl chloride by heating it in conjunction with ozonised 90 per cent methyl alcohol. Lawson[14] recommended the application of small amounts of benzoyl peroxide for polymerisation in a chlorbenzol medium carried out in a tin-lined vessel under pressure of 15 atmospheres at 118° C.; the polymer is insoluble in toluol.

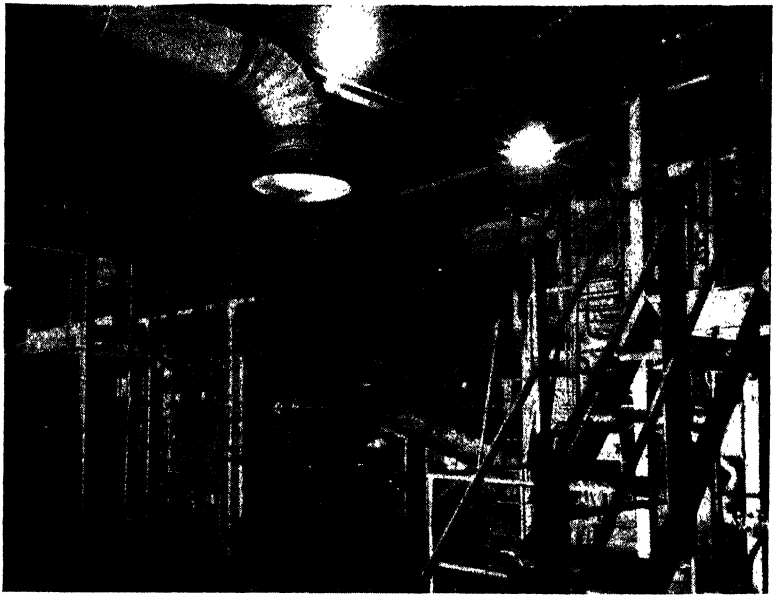


Fig. 178. General view of mixing equipment for polyvinyl chloride, showing Banbury mixer and conveyor belt leading to the sheeting rolls

Alpha-polymer may be obtained by polymerising vinyl chloride at 90°–120° C. in the following solvents: methyl alcohol, dichlorethane, chlorbenzol, ethyl acetate, benzol, acetone, toluol, in presence of benzol or barium peroxides, or ozone, as catalysts.

The polymerisation may be accomplished in a solution of methanol, ethanol, pentane, hexane, acetone, aromatic hydrocarbons, such as toluol, xylol, in presence of oxidising catalysts at 40° C.

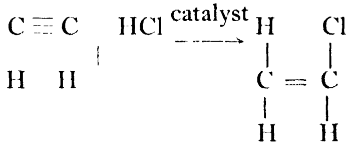
The polymerisation when carried out in alcohol or benzene results in finely dispersed polymeric products.

Emulsion polymerisation is now the predominating process in all parts of the world. Thus, in the I.G. plants at Ludwigshafen and Schkopau continuous emulsion polymerisation was in operation. At Bitterfeld batch emulsion polymerisation was the method used. For electrical grades, the soluble electrolytes had to be washed out and the powders dried. The German methods are given because full details of their production are known.

Manufacture of Vinyl Chloride and Polyvinyl Chloride at I.G. Farbenindustrie, Schkopau.[29] Vinyl chloride and polyvinyl chloride are produced along the following lines at the I.G. Farbenindustrie at Schkopau.

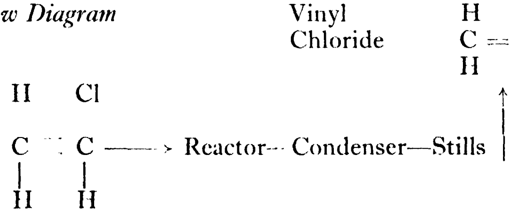
1. *Vinyl Chloride*

Chemistry



$$\underset{H}{C}\equiv\underset{H}{C} \quad HCl \xrightarrow{\text{catalyst}} \overset{H}{\underset{H}{C}}=\overset{Cl}{\underset{H}{C}}$$

Flow Diagram



The materials used at the Schkopau plant are:

Acetylene: 98·0 per cent acetylene made from CaC_2 at Schkopau. The acetylene must be dry.

HCl: 95–98 per cent HCl made by burning hydrogen and chlorine at Schkopau. It must be dry.

Catalyst: Mercuric chloride on activated carbon. 8 to 14 mesh carbon is soaked in a solution of mercuric chloride and dried. Analysis on dry basis, 90 per cent carbon and 10 per cent mercuric chloride.

Calcium Chloride: A 25–30 per cent solution of calcium chloride for refrigeration purposes.

2. *Description of Process.* The incoming acetylene is thoroughly dried with KOH and the hydrochloric acid with concentrated H_2SO_4. The reactants must be free of moisture since the catalyst life was dependent on this feature. The reaction vessel is constructed entirely of iron and is approximately 10 ft. high and 6 ft. in diameter. It is mounted vertically and is filled with catalyst tubes, each 10 ft. long by 2½ in. inside diameter. Each furnace contains an estimated 100 to 150

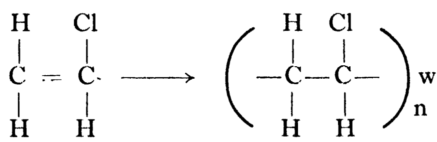
tubes. Eighteen such units are required for the given production of 3,500 to 4,000 tons per month. The temperature is accurately controlled by circulating cooling water around the catalyst tubes. The operating temperature with fresh catalyst is 120° C. This is gradually increased to as high as 200° C. over a period of six months to one year. The catalyst is then discarded. It cannot be reactivated, but the mercury is recovered.

When a new furnace is put into operation all air is replaced with nitrogen, the furnace is brought up to temperature, and the acetylene and hydrochloric acid introduced. The reaction is highly exothermic and good cooling is necessary. It is common practice in Germany to use water for heating or cooling even at temperatures as high as 250° to 300° C. It is extremely simple to remove the heat from the water by flashing off steam.

HCl is always carried in 10 per cent excess over the acetylene. The reaction is at atmospheric pressure. Pressure drop through the catalyst is less than 1 lb. The acetylene in the reaction mixture is approximately 10 per cent. Excess HCl is removed with water. The vinyl chloride is cooled and condensed by a spray of 25 per cent $CaCl_2$ solution at —40° C. Distillation is carried out in two ring packed columns 20 ft. high by 36 in. diameter. The first still takes vinyl chloride plus acetylene over the top and residual high boiling chlorinated compounds out of the bottom. (Mostly unsymmetrical ethylene dichloride.) The second takes acetylene overhead and very pure vinyl chloride off the bottom. Yield on acetylene is 96–98 per cent; on HCl, 80–90 per cent. The vinyl chloride is stored in iron tanks underground at —40° to —50° C. No inhibitor is added. The vinyl chloride is shipped in 60,000-lb. iron tank cars without inhibitor. They are not insulated, but do have a wooden housing over them to protect them from the sun. Nitrogen is always used as an inert gas over the vinyl chloride.

3. *Polyvinyl Chloride* (*PCU*)

Chemistry



$$\underset{H}{\overset{H}{C}} = \underset{H}{\overset{Cl}{C}} \longrightarrow \left(-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}- \right)_n$$

where n = 700 approx.

D. *Chemicals*

(*a*) Vinyl chloride: Pure vinyl chloride made at Schkopau containing no known impurities. Must be free of acetylene and higher chlorinated compounds.

(*b*) Mersolate: The sodium salt of the product formed by reacting SO_2 and Cl_2 with a long chain (C_{15} to C_{20}) hydrocarbon made at Leuna.

(*c*) Sodium persulphate: Technical.
(*d*) Hydrogen peroxide: 40 per cent in water, shipped and stored in carboys.

E. *Description of Process*

Two types of polymer are made. One for electrical applications is polymerised with hydrogen peroxide catalyst. The second is polymerised with $Na_2S_2O_8$ catalyst, and is used for all other purposes. Polymerisation time is shorter when $Na_2S_2O_8$ is used, and for this reason is preferred when electrical properties are not important. Two methods for drying the polymer are used at Schkopau—spray-drying or coagulating, followed by filtering, washing, compressing, and finally drying with hot air. Two hundred tons per month can be produced by the second method.

The polymer process is continuous in contrast to the batch method practised at Bitterfeld. The continuous process gives a more uniform product, having a higher molecular weight and involving simpler plant.

Each reactor is a jacketed, vertical glass-lined cylinder 25 ft. by 5 ft. in diameter with a paddle agitator in the top seven feet. Ratio of reactants are as follows:

35 per cent vinyl chloride
3 per cent mersolate (based on vinyl chloride)
0·5 per cent hydrogen peroxide or
0·1 to 0·2 per cent sodium persulphate } based on vinyl chloride
Balance water

Three streams are metered into the top of the reactor:

(1) The mersolate and water which were previously mixed.
(2) The vinyl chloride.
(3) The catalyst dissolved in a small quantity of water.

Emulsification takes place in the first or upper few feet of the reactor. The temperature is accurately controlled at 45° C. from top to bottom of the reactor by means of a water jacket on the reactor. Reaction time is 3·5 hours with sodium persulphate and 5 hours with hydrogen peroxide. From the bottom of the reactor the emulsion (now 85 per cent polymerised) is pumped to a helical spiral vacuum evaporator where the excess monomer is flashed off, condensed, and recycled to the polymerisers. The evaporator is about 15 ft. high and 8 ft. in diameter, jacketed and heat insulated. Exposed parts are of nickel. It is operated at 100 mm. pressure. As the emulsion flows slowly down the spiral path all excess monomer is evaporated without breaking the emulsion. The spiral trough is about 18 to 20 in. wide and 3 to 6 in. deep, and makes one spiral in 12 to 18 in. One evaporator has capacity for all production to the spray dryer.

The emulsion free of monomer is now either spray-dried or coagulated and dried by conventional methods. When the coagulation method is used aluminium sulphate is added in a glass-lined kettle, the suspension settled, decanted, and filtered on a continuous (Oliver-type) filter approximately 6 ft. in diameter with a 3-ft. face. The powder is washed on a belt as it passes to a second similar filter. Soda (0·2 to 0·5 per cent) is added at this stage as a stabiliser. The damp powder is then compacted on an aeroform continuous press. The resulting pellets are dried at 80° C. on a link screen belt, ground to a fine powder, and packaged in paper bags (50 lb.) for shipment. 0·5 per cent alpha phenyl indole or 0·5 per cent diphenyl urea are occasionally used for stabilisers.

Production of PVC by Batch Polymerisation. There are a number of interesting features in connection with the batch polymerisation of P.V.C. as carried out at Bitterfeld.

Large autoclaves 40 ft. long by 3 ft. 3 in. internal diameter are used. They are water-jacketed and lined with glass or nickel. The autoclave is charged with an aqueous phase and the vinyl chloride consisting of the following:

(*a*) *Aqueous* phase.

1,000 gallons of softened water
400 lb. soap
40 lb. 40 per cent hydrogen peroxide

These are stirred together until the soap dissolves.

1,100 gallons of vinyl chloride

The autoclave is charged and is then rotated, the temperature being brought up to 40° C. by means of warm water in the jacket. It runs in this way for about 24 hours, the temperature and pressure being continuously watched. At the end of the process the pressure drops to ½ atmosphere and the pH of the aqueous phase falls from 6·8 to 5.

The P.V.C. is then spray-dried and batched.

Properties of Polyvinyl Chloride. Polyvinyl chloride is odourless, tasteless, chemically inert, and non-inflammable, except when held in direct contact with flame. It is available as a fine white powder. Its specific gravity is 1·33. It shows thermoplastic properties. It is almost insoluble in all cold solvents, although readily soluble in hot chlorinated hydrocarbons, such as ethylene dichloride or monochloro-benzene. Heat and light stability are poor. The high softening temperature of this resin makes milling and moulding difficult because inadequate heat stability prevents the use of temperatures high enough to relieve strains. Tensile and impact strength and other mechanical properties of the pure resin are therefore unsatisfactory.

As in the case of other vinyl resins, the average molecular weight of polyvinyl chloride can be varied over a wide range, with corresponding variations in physical properties. According to Buchmann[6] polyvinyl chloride of low molecular weight, e.g. 20,000 to 30,000, is unsuitable for plastic purposes, but can be used for coatings and impregnation. For plastic applications the molecular weight must be high, of the order of 60,000 to 130,000. For industrial use polyvinyl chloride is always plasticised.

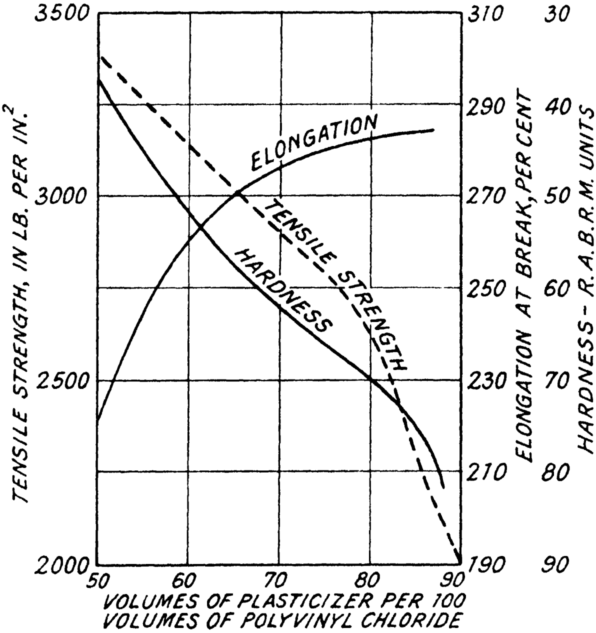


Fig. 179. Properties of polyvinyl chloride compositions

The Germans have, however, developed methods for producing a range of products, including film, from straight unplasticised polyvinyl chloride. Unplasticised polymer could be extruded, calendered, or press laminated. It has outstanding strength, lightness, and chemical resistance.

Unplasticised P.V.C. Polyvinyl chloride has not found many uses in the straight and unplasticised form owing to its comparative lack of flow and the fact that it decomposes very readily at moulding temperatures. Thus polyvinyl chloride alone may be moulded at temperatures above 120°C. under high pressure exceeding 500 lb. per sq. inch. The moulding obtained is very hard and quite brittle. In fact, used without plasticisers its mechanical properties are more closely related to those of celluloid or hard rubber. There have been profound developments in this aspect of P.V.C.

Unplasticised P.V.C. has up to now only been extensively used in Germany. The material is very promising. Production is proceeding in other countries. Successful production depends on the availability of a suitable grade of polymer.

Unplasticised P.V.C. has two main fields of application in Germany, the first as sheets, rods and tubes for chemical engineering purposes known as Vinidur, and the second as a specially prepared film called Luvitherm.

Vinidur. Vinidur consists of unplasticised P.V.C. with a K-value of 60 containing a small amount of lubricant and stabiliser. The stabilisers used include sodium carbonate, alpha phenylindole and diphenyl thiourea; the lubricant, added to facilitate processing, is ceresin wax which has replaced octadecyl alcohol.

The processed polymer is a translucent material of density 1·38 with normally a reddish-brown hue, the intensity of which depends upon the temperature and duration of processing.

Vinidur has a number of chemical engineering applications; it can be used in equipment where low temperatures, between —10° C. and —50° C. are encountered, and also where good resistance to alkalis, concentrated hydrochloric acid, hydrofluoric acid, sulphuric acid (up to 85 per cent) and nitric acid (up to 55 per cent) is required.

It cannot however be used in contact with any material which is likely to act as a gelling agent or plasticiser, e.g. aromatic and aliphatic hydrocarbons or their derivatives. It is of course also unsuitable for chemical plant dealing with esters.

Fabrication. Vinidur is normally fabricated in sheet and tube form. It can be sawn, drilled, turned, milled, etc., in a manner similar to that adopted for light metals; in fact, the I.G. compared the technique for working this material with that used for machining brass. High speed tools are recommended. It should, however, be remembered that it has its limitations as it is a thermoplastic material. During machining operations scrap material is normally removed by means of compressed air which serves the double function of cooling the Vinidur and preventing it becoming plastic.

Tubes of normal diameter are fabricated by extrusion methods, the Eckert and Ziegler double screw extruder being considered the most satisfactory machine for this purpose. A further method of fabrication is by means of a ram extruder.

The tubes can be bent to any angle by filling them with sand, inserting bungs in the ends so that the sand is kept as tightly confined as practicable, and then heating the tubes to a temperature of 130° C. by means of hot oil, hot air or a broad flame. At this temperature the material becomes soft enough for the tubes to be manipulated into the required shape.

Welding. Vinidur can be welded easily by means of a hot air gun which consists essentially of a stream of compressed air heated by a coal gas flame or electrical element. The height of the flame and the pressure of the compressed air regulate the temperature of the outlet gas which is kept at 200–230° C.; care must be taken to ensure that this temperature is not exceeded, otherwise the Vinidur will char.

The technique of welding Vinidur is similar to the autogenic welding of metals. It is claimed that the strength of welds obtained is 95 per cent of that of the original material, but in practice the welds are assumed to be 50 per cent of the strength of the Vinidur itself.

Friction welding can also be used to join Vinidur sections together. The two pieces to be welded are jigged on a lathe and then brought together while one sample is rotating at high speed.

Uses in Industry. When Vinidur pipes are used in chemical plant, adequate care must be taken to ensure that they are properly supported especially where there is a possibility of the working temperature exceeding 50° C.

Steel containers for use at ordinary temperatures, such as storage vessels for hydrofluoric acid, can be coated with Vinidur in the form of foil. The metal is first cleaned by means of a sand blast or sandpaper and then three coats of a 10 per cent solution of chlorinated P.V.C. in methylene dichloride are applied to the steel surface. The Vinidur foil is coated with a 20 per cent solution of chlorinated P.V.C. in methylene dichloride. Finally heat is applied to the uncoated side of the steel until its temperature reaches 130° C., whereupon the coated side of the foil is pressed against the coating on the steel and the whole left to cool.

Vinidur is also used for moulding battery boxes, etc. To obtain maximum impact strength in the finished moulding the pressing temperature must be maintained between 110° and 130° C.

Vinidur sheeting is normally prepared by calendering on a four-bowl machine. The maximum thickness of smooth sheet which can be produced by a four-bowl calender is 0·4 mm. Thicker sections are made by pressing such sheets together in a multi-daylight press at a temperature of 180° C. By this method the Germans could make a sheet up to 20 mm. thick.

Luvitherm. Luvitherm film is manufactured by calendering unplasticised P.V.C. and subjecting the resultant film to a stretching action produced by winding off the material on to rolls at a faster rate than it is being supplied from the calender. The stretching is carried out in two stages and the final thickness of the Luvitherm film is 25 to 35 μ. This process tends to orientate the P.V.C. molecules with the result that the film has a high tensile strength in the direction of stretching.

Luvitherm film is normally used in the fabrication of sound-recording tape, and also in packaging and insulation purposes. As a wrapping insulation for cables it saved not only the large quantities of P.V.C. normally used in extrusion coating processes, but also plasticisers, both of which were in extremely short supply in Germany.

The Germans produced bristles and canelike materials by extruding P.V.C. powder with a little stearyl alcohol. It was extruded at 160° C. at a speed of 30–40 feet per minute. It was stretched 225 per cent by one pair of rollers working in water at 90° C. and a further 25 per cent by a second pair of rollers at 20° C.

Compounded P.V.C. P.V.C. is generally plasticised and compounded. There are numerous proprietary materials available.

Much of the latest knowledge on the subject has come from the intensive work carried out jointly by cable manufacturers in Great Britain, and leading plasticising concerns. Many leading developments have resulted from this work.

TABLE 122

EFFECT OF SIX PLASTICISERS ON PHYSICAL PROPERTIES OF "KOROSEAL"[20]

Plasticiser	Hardness	Tensile Strength		Elongation	Tear Resistance	Heat Loss	Flexibility Limit
		Kg./sq. cm.	Lb./sq. in.	%	Kg./cm.	%	°C.
A .	73	156	2,220	350	61·2	2·8	−3
B .	76	146	2,070	365	63·0	6·3	−1
C .	84	160	2,280	325	77·6	26·3	+9
D .	68	94	1,340	380	42·1	32·3	−24
E .	69	112	1,590	395	42·0	6·6	−22
F .	71	112	1,590	340	52·3	8·0	−17

The earliest commercial compound Koroseal was developed by Semon,[21] who started work on the problem in 1927, working upon the principles laid down by Ostromislensky. Semon found that polyvinyl chloride was insoluble at ordinary temperatures in practically every known solvent. In his patent in 1933 he suggested chlorinated naphthalene, tricresyl phosphate, and various nitro-derivatives. On the other hand, he found that at high temperatures it was swelled and dissolved by tricresyl phosphate. Similar behaviour is shown by a few other solvents such as furfural, nitro-benzene, etc. Apart from these it is soluble only in very small concentrations in solvents such as cyclohexanone, dioxan, mesityl oxide, chlorinated hydrocarbons, isophorone, etc.

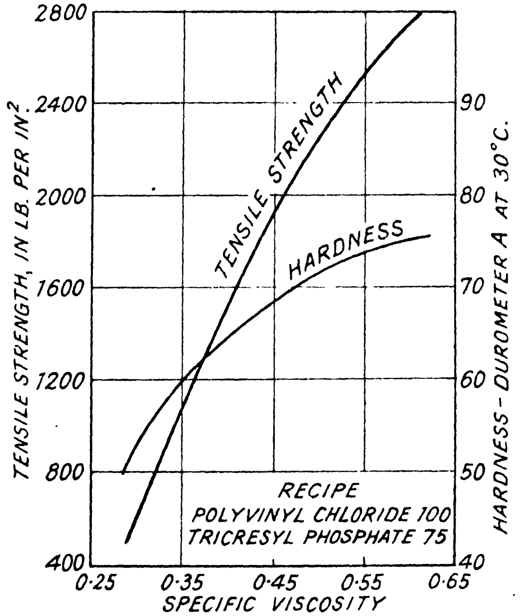


Fig. 180. Variation of properties of polyvinyl chloride with molecular weight

On the basis of this work he was able to develop a method for plasticising the material with tricresyl phosphate. This can be done by mixing polyvinyl chloride with tricresyl phosphate, at high temperature, either in an internal mixer or on open rolls.

This is the technique now generally practised in preparing composition of polyvinyl chloride. All components are premixed in a dry paddle mixer. The material is then fed on to the mixing mill. Temperatures above 150° C. are used, and a time of about thirty minutes is required for adequate mixing. Mixing is also carried out in internal mixers of the Banbury type. It can also be achieved in the Baker Perkins type of mixer.

When this procedure is carried out, a tough rubber-like elastic mass is obtained, which, however, is thermoplastic, and which can be processed or fabricated by all the methods normally used with rubber. It can be extruded, moulded, or sheeted. Its properties are almost entirely dependent upon the amount and nature of the plasticiser which is added.

Processing of Polyvinyl Chloride. The white powder is the synthetic resin used for the preparation of commercial plastics. Leading products include *Corvic*, made by Imperial Chemical Industries (Plastics), Ltd., *Vinylite QYNA*, made by Carbon and Carbide Corporation; *Geon*, made by the B. F. Goodrich Co.

Geon has molecular weight of 85,000, while Corvic has molecular weight of 72,000.

The essential make-up of a polyvinyl chloride plastic includes the following ingredients:

(*a*) Resin
(*b*) Plasticiser
(*c*) Stabiliser
(*d*) Lubricant.

Not quite so essential, but nevertheless widely used, are: pigments, fillers, and extenders.

A number of other plasticisers are now known, which are used to convert polyvinyl chloride into plastic masses.

Plasticisers for Polyvinyl Chloride. Among materials employed as plasticisers, esters are generally the best, while many ketones and sulphur compounds are satisfactory.

The outstanding types of plasticisers for this purpose are tricresyl phosphate, dioctyl phthalate, dibutyl phthalate, and diethyl phthalate. Recent technical applications have made it essential that polyvinyl chloride composition should retain its flexibility at very low temperatures. As a result the older types of plasticisers have been to some extent replaced by materials such as dihexyl phthalate, dioctyl phthalate, dibutyl sebacate, butyl acetyl ricinoleate, etc. All these in suitable quantities, about 50 parts per 100 polymer, give compositions which will not crack even at temperatures of —70° C.

Many plasticisers have very limited compatibility with polyvinyl chloride. This is shown by the manner in which they bloom or sweat out to the surface. Nevertheless, many of these impart desirable characteristics to the material when used as extenders for the more compatible materials. Materials of this type are often known as extenders, although this really means extenders of the plasticisers, not the polymer. Notable materials are chlorinated paraffins (e.g. *Cereclor*), high boiling aromatic distillates from petroleum, etc. In connection with aromatic distillates compatibility is found to depend on the degree of aromaticity; the more aromatic, the better the compatibility.

Brous and Semon[5] showed how variation in the amount of a single plasticiser gave a remarkably comprehensive range of properties from hard material comparable to ebonite, down to the consistency of the softest of soft vulcanised rubber. Variation between 10 and 60 per cent of tricresyl phosphate in a polyvinyl chloride mix gave tensile strength varying from 9,000 to 1,000 lb. per sq. inch, elongation from 2 to 500 per cent, and shore hardness from 100 down to 15.

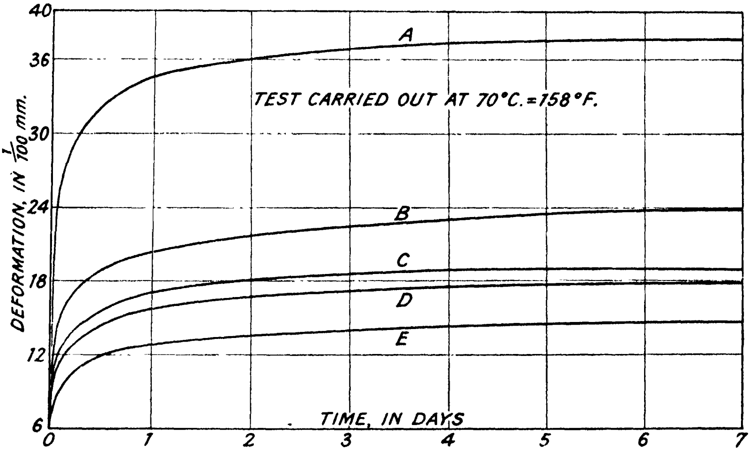


Fig. 181. Thermal deformation of polyvinyl chloride compositions

Schoenfeld, Browne, and Brous[20] have shown the different properties obtained from Koroseal prepared with a number of different plasticisers.

At high temperatures, such as those used in processing, polyvinyl chloride tends to decompose when in contact with metals such as iron, zinc, etc.

Hydrogen chloride is formed, and the compositions darken. There is a tendency for porosity, and materials progressively become hard and brittle.

It is necessary to add stabilisers in order to protect the material from decomposition, and in general lead salts are used for this purpose. They have proved to be most effective. Lead carbonate, litharge, lead chromate are typical stabilisers, being used in quantities of the order of 5 per cent of the weight of polymer. Other widely used materials are white lead, red lead, lead silicate, lead naphthenate, and lead resinate. Small amounts of the order of 1 per cent lubricant material are added, typical ones being calcium stearate or ethyl palmitate.

Quattlebaum and Nofflinger[16] proposed the use of 1 per cent of maleic anhydride as stabiliser for polyvinyl chloride.

TABLE 123

EFFECT OF AMOUNT OF PLASTICISER ON PHYSICAL PROPERTIES OF "KOROSEAL"[20]

Vol. Tri-cresyl Phos-phate[1]	Hard-ness[2]	Tensile Strength[3]		Elonga-tion[4]	Tear Resist-ance[5]	Oil Ex-tract[6]	Gaso-line Ex-tracts[7]	Heat Loss[8]	Flexi-bility Limit[9]
		Kg/. sq. cm.	Lb./ sq. in.	%	Kg./cm.	%	%	%	°C.
50	96	233	3,320	190	142·8	0·3	−4·8	1·0	20
75	80	211	3,000	270	78·5	2·5	8·8	1·3	7
100	68	147	2,100	330	53·6	6·3	15·9	1·3	−5
150	49	98	1,400	490	28·6	17·9	19·7	1·4	−22

[1] Per 100 volumes of polyvinyl chloride.

[2] Shore Durometer, type A, 30° C.

[3] Force required to break standard dumb-bell at 30° C.

[4] Ultimate elongation at 30° C.

[5] Force (in kg. per cm. thickness) required to tear standard sample at room-temperature.

[6] Percentage loss in weight after immersion in oil for 14 days at 50° C.

[7] Percentage loss in weight after immersion in motor gasoline for 14 days at room-temperature.

[8] Percentage loss in weight after heating in an air-circulating oven for 14 days at 105° C.

[9] Temperature at which a standard strip under a constant weight will bend through an angle of 30° in 2 minutes.

Stabilisation of German polymer is effected by means of 0·2 per cent of either α-phenyl indole or diphenyl thiourea.

The material may be further compounded by the addition of a wide variety of filling materials. These tend to make the material shorter and reduce the rubber-like properties. Fillers do not enhance the tensile strength of compositions. The quantities used up to the present time are not very great, up to 25 per cent, for beyond a certain limit the rubber-like properties disappear although toughness is retained. The effect of heavy loading is to make the material hard and short; the valuable flexibility at low temperature is adversely affected. Different fillers naturally have different effects. Channel black and silica improve the tensile strength. Softer blacks improve tearing resistance, while other fillers such as clay, whiting, etc., improve oil resistance.

Fig. 182. Plant used for mixing polyvinyl chloride compounds[26]

Fig. 183. Polyvinyl chloride compound from the Banbury mixer being discharged on the sheeting rolls[26]

Heavy Compounding of Polyvinyl Chloride. Polyvinyl chloride when suitably plasticised will take up large proportions of fillers and pigments. Loadings up to 300 volumes of the polymer can be incorporated. The products obtained have interesting properties either leathery, rubbery, or hard and rigid according to requirements. Leathery materials have great prospects for products such as trunks, bags, and so on.

Fig. 184. Polyvinyl chloride compound leaving the sheeting rolls in the form of a strip. It can be used as such, or may be reduced to granules on a disintegrated machine

Rubbery materials seem promising for floor coverings, counter tops, etc. One of the outstanding factors is the ease of production and the excellent colour scope. Rigid materials have found many uses.

Influence of Other Ingredients. Polyvinyl chloride is not very compatible with many gums, waxes, and oils. Compatible materials include chlorinated diphenyls, coumarone resins, rosin, tung oil, coal-tar, and asphalt.

Great progress has been made in the incorporation of softening materials into polyvinyl chloride, which are not in themselves plasticisers. Among materials which come into this category are high boiling aromatic distillates obtained from petroleum, coumarone resins, rosin, factices, and so on. All these materials exert an appreciable softening effect.

High boiling aromatic distillates have proved extremely satisfactory.

TABLE 124

EFFECT OF HIGH PIGMENT LOADINGS[20]

Polyvinyl chloride	100 vol.
Tricresyl phosphate . .	89 vol.
Pigment	As specified

	Thermax						Whiting				
Vol. of Pigment	Hardness	Tensile strength		Elongation	Tear Resistance	Hardness	Tensile strength		Elongation	Tear Resistance
		Kg./sq. cm.	Lb./sq. in.	%	Kg./cm.		Kg./sq. cm.	Lb./sq. in.	%	Kg./cm.
0 .	74	169	2,400	335	62·5	74	169	2,400	335	62·5
50 .	84	155	2,200	200	94·6	85	122	1,730	225	58·9
100 .	92	169	2,410	95	67·9	92	92	1,310	120	46·4
150 .	95	156	2,230	45	30·4	95	70	1,000	85	26·8
200 .	96	151	2,140	25	8·9	96	67	960	50	19·6

Large proportions may be added, exceeding the amount of polymer. The products prepared in this manner have many useful properties.

They are elastic, have high tensile strength and elongation, and excellent flex resistance. Polyvinyl chloride compositions, suitably compounded with tricresyl phosphate or dibutyl phthalate, have outstanding flexing properties. The best types have shown flex resistance of 3,000,000 flexures, several times superior to a comparable rubber composition. They are highly resistant to the effect of oils and solvents. They take up only small quantities of water, in this respect being superior to rubber even after very prolonged immersion. They are very resistant to ageing.

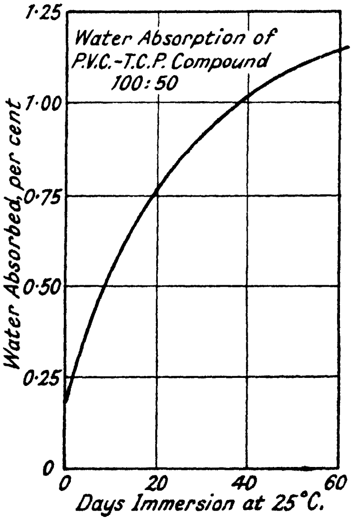


Fig. 185. Water absorption of polyvinyl chloride

Elastic Behaviour of Polyvinyl Chloride Compounds. Polyvinyl chloride compositions are incompressible. High elongation, can be achieved up to 500 per cent. At ordinary temperatures the plasticised material will return to its original shape after any distortion up to the breaking point. When distorted, however, it does not snap back immediately to

Fig. 186. After being disintegrated, "Welvic" polyvinyl chloride compound is passed over a magnetic separator and then discharged on to a cooking tray[26]

Fig. 187. Granules of "Welvic" polyvinyl chloride compound as used for extrusion[26]

its original shape as does rubber. Its recovery from either elongation or compression is slow. When slightly distorted it recovers in a second or so. More severe distortion may require several seconds before recovery, and if it is stretched to a point just below its elastic limit, it may not recover its original size for several minutes. But eventually it always comes back. Under compression at low temperatures the permanent set or deformation is slight, varying with the composition. At high temperature the set becomes considerable as plastic flow occurs, which far exceeds the ability for elastic recovery. They have some disadvantage, the chief being that they soften at comparatively low temperatures, about 80° C., when plastic flow becomes evident. However, if applied with due appreciation of the temperature limitations, they are excellent materials.

Chemical Properties of Polyvinyl Chloride. These compositions of polyvinyl chloride are unaffected by ozone and oxygen, and by virtue of their chlorine content they do not support combustion.

These materials are very inert chemically, and are consequently highly resistant to chemical corrosion. They resist attack by ozone for indefinite periods. Oxygen does appear to have some influence on the material when it is heated for a long time at temperatures of the order of 160° C. In connection with resistance to chemicals and solvents the nature of the plasticiser must always be considered in case it should be affected by the chemicals concerned. They withstand strong acids such as sulphuric acid, and nitric acid for long periods, and they also withstand the effect of strong alkalis. For example, they are used for making transparent connections in chemical equipment.

Polyvinyl chloride compositions have excellent resistance towards oils, solvents and greases. They are unaffected by mineral oils, petrol, and so on. The only point about these is the tendency for the extraction of plasticisers; in contact with such solvents a suitable plasticiser should be employed. This factor is of some significance in the product of non-inflammable petrol hose where polyvinyl chloride is often used as a lining. They are not affected by alcohol, glycerine, glycols, etc. They are swelled by chlorinated solvents, by nitro solvents, and by ketones.

Polyvinyl chloride compositions are admirably suited for many uses in the cable industry. They have been widely used as a replacement for rubber.

In Great Britain, the cable industry is the leading user of polyvinyl chloride, and has made numerous important contributions to the technique. Suitably compounded compositions have high dielectric strength, are resistant to ozone, and can be compounded to give lower power factor. The electrical properties have been exhaustively studied. Barron, Dean, and Scott[1] have described these activities. The use of polyvinyl chloride for every form of wire and cable covering is spreading rapidly. It has a considerable usage for cable covering in the United States, in Britain, in Germany, etc.

Coated wire is fabricated simply by extruding the plasticised material round the wire to the desired dimension. It offers certain advantages over rubber, e.g. no vulcanisation process is required. There is a large range of bright colours available, either opaque or transparent. The excellent resistance to solvents and corrosive influences also commend the material for cable application. The material will burn when in a flame but does not otherwise burn; in fact it tends to extinguish flames. Small bores and thin wall thicknesses may be obtained.

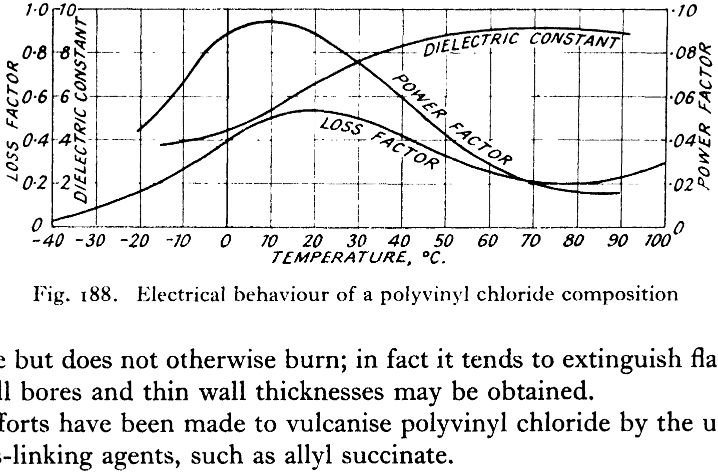


Fig. 188. Electrical behaviour of a polyvinyl chloride composition

Efforts have been made to vulcanise polyvinyl chloride by the use of cross-linking agents, such as allyl succinate.

Electric Characteristics. According to Barron, Dean, and Scott, with the exception of electric strength, the electrical characteristics of polyvinyl chloride are so dependent upon the polymer, plasticiser, extender, filler, etc., employed that a careful check must be made of the compound to determine whether the specified requirements have been met. They showed that the resistivity of compounds which have been plasticised to give −30°C. cold flexibility ranges from 1×10^{10} to 1×10^{12} ohms/cm. cube at 20°C. If less plasticiser is employed (cold flexibility −25°C.), values of 1×10^{12} to 1×10^{14} may be obtained. Further raising of the cold-flexibility temperature coupled with the use of the highest electrical grades of polymer, plasticiser, etc., may enable the resistivity to be raised somewhat above 1×10^{15} at 20°C. This comparatively low maximum value is coupled with a steep resistivity/temperature characteristic which reduces the resistivity to 1/100th about of its value for a rise in temperature of 50°C. It will therefore be realised that polyvinyl chloride insulated cables are not particularly interesting from the insulation-resistance point of view. Fortunately this characteristic is seldom of real practical value in service. For thermoplastic cables which in service require high insulation resistance a non-polar material such as polythene must be employed.

Similarly, the dielectric loss of the material is high and extremely variable with temperature and frequency. By careful selection of plasticiser and other ingredients, compounds may be produced having reasonable dielectric power factors (e.g. 0·05–0·06). In general, however, such selection imposes serious limitations on the mechanical properties of the compound.

TABLE 125

ELECTRICAL CHARACTERISTICS OF POLYMERS

	Polyvinyl Chloride	Polyvinyl Chloride-acetate	Poly-vinylidene Chloride
Resistivity (ohms/cm.) . . .	10^{14}	10^{15}	10^{15}
Breakdown voltage (volts per mil.) .	750	450	1,000
Power factor (50 cycles) . . .	0·1	0·01	0·02
Dielectric constant . . .	6	3·4	4

The conclusion must be reached that, except during war emergency, polyvinyl chloride is unlikely to be used as an insulant at frequencies greatly in excess of 2 kc/s.

Similar remarks apply to the permittivity which for an insulating grade at 20° C. works out in general at 6 to 8. Special compounding can achieve values of 4·5 to 6 with the limitations mentioned above. There is also a pronounced temperature coefficient for permittivity.

Extrusion of Polyvinyl Chloride. Polyvinyl chloride is extruded for flexible tubings and conduits of every description and every degree of flexibility. It is employed to make diaphragms, packings, seals, and gaskets. By virtue of its corrosion resistance it is employed for lining metal tanks.

The Germans have carried out extrusion of quite large sections by using piston extruders as distinct from screw extruders. A charge of hot milled compound is loaded in the feed-box and extruded. Tubes up to 6 in. diameter were made in this way.

According to Brous,[4] polyvinyl chloride compositions may be bonded to metals by covering the metal with a coating of chlorinated rubber solution, applying a solution of polyvinyl chloride to this and then attaching the plastic.

Another method uses two adhesives, one for coating the metal—based on polyvinyl acetate, followed by a solution of polyvinyl chloride itself.

It is used to make transparent tubes for factory and laboratory applications. It is extensively used for machine parts in the textile industry, where its flexibility coupled with oil resistance, make it highly valued.

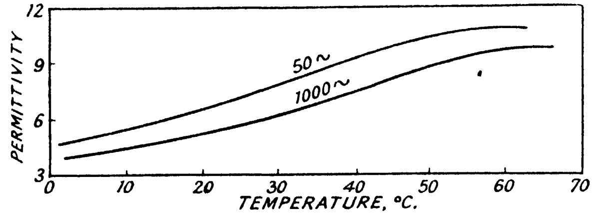


Fig. 189. Influence of frequency on permittivity of polyvinyl chloride compositions

P.V.C. Sheet. In the form of calendered sheet, polyvinyl chloride is finding wide application. Transparent, translucent and coloured sheets of every description are available. For example, it provides material having suitable characteristics for artificial leather, and a wide field of application is foreshadowed and is being energetically exploited.

The calender consists of two or more massive steel rolls generally mounted vertically. The rolls are heated by steam and can be cooled by passing water through. The distance between the rolls can be very accurately controlled. The temperature of the rolls is very closely controlled. The most widely used type is illustrated. Very smooth wide sheets of material of uniform thickness are obtained by its use.

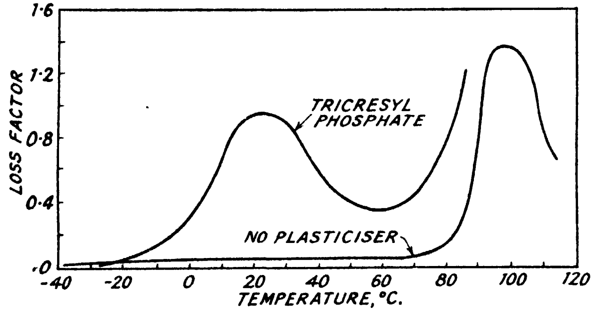


Fig. 190. Influence of plasticiser on loss factor of polyvinyl chloride compositions

Polyvinyl chloride compositions may be calendered in a manner similar to that used for rubber. The polyvinyl chloride composition is formed into a soft dough on hot mixing rolls. It is then fed on to the calender, which is at a much higher temperature than with rubber. Temperatures are of the order of 125–135° C. Sheetings from 0·0015 inches up to 0·125 inches can be made. It is difficult to ply calendered polyvinyl chloride owing to lack of adhesion. Thick sheets of small sizes may be moulded.

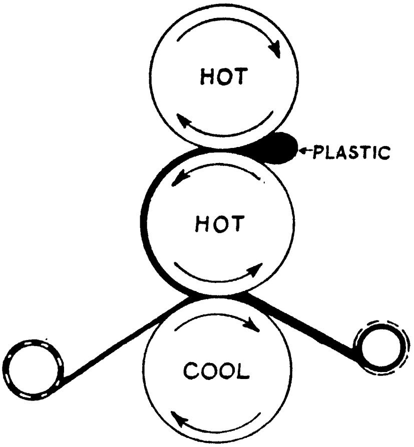


Fig. 191.
Cross-section view of calender

When P.V.C. polymer, the fine white powder of commerce, is mixed with usual proportion of plasticiser, it normally forms a damp powder. If, however, the particle size of the powder is sufficiently small then a uniform dispersion is obtained viscous but quite fluid in character. In this form it can be moulded, cast, coated, or dipped. The pastes obtained from these paste-forming resins have acquired great commercial

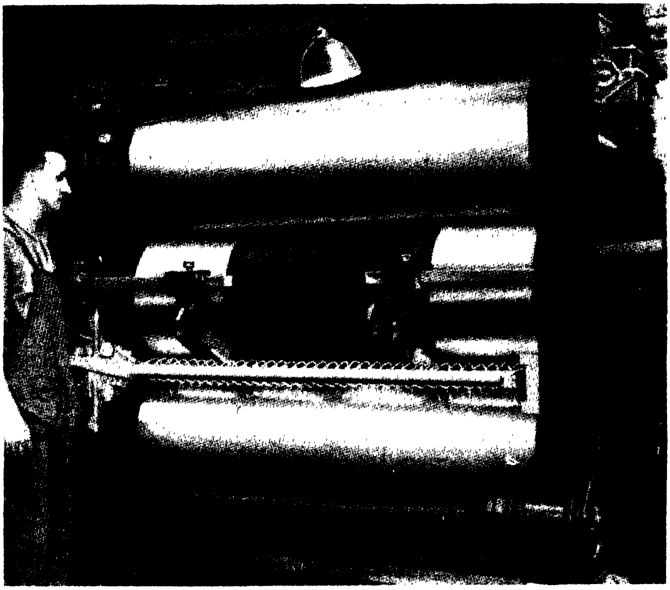


Fig. 192. A calender in use[27]

significance. The reason is obvious inasmuch as its use eliminates the need for heavy and costly mixing and processing equipment for making similar products. Pastes are being used to make film, coated fabrics, printers rolls, shoe soles, toys, and so on.

P.V.C. paste consists of the polymer dispersed in plasticiser. At ordinary temperatures it maintains the paste condition for very long periods. But if the temperature is raised then the plasticiser begins to gel the P.V.C. The process is known as gelation. The behaviour is comparable to the behaviour of gelatin in water. This blending of the two ingredients results in a tough, solid flexible mass comparable in all respects with the product obtained from the same ingredients by the standard mixing process.

TABLE 126

TYPICAL PROPERTIES OF GEON 100—X—210 WITH VARYING AMOUNTS OF RESIN AND PLASTICISER

Geon 100—X—210	45	50	55	60	65	70
Dioctyl phthalate	55	50	45	40	35	30
Hardness (after fusion) Durometer A.	50	55	65	70	80	90
Initial viscosity centipoise	1,000	2,900	3,000	3,500	7,500	87,000

To obtain the best properties it is necessary to reach the correct gelling temperature, i.e. it must exceed 150°C. The fusion of the resin and plasticiser then gives material having the best physical properties.

A paste-forming polymer is one which is capable of forming a free flowing paste with ordinary proportions of plasticiser. The particle size of the Geon type is said to range from 1 to 30 micron with a mean diameter of 8 to 10 microns. It is possible to take ordinary commercial grades of P.V.C. and grind them to suitable particle size for paste production. A paste resin is designed to give a fluid and easily applied thermoplastic material. Thus, the choice of plasticiser is extremely important. Selection should be limited to those that give a low viscosity and a slow rate of solvent action at room temperature, and when heat is applied, plasticise the resin rapidly to produce a solid fused mass. Other properties to be considered when choosing a plasticiser are low temperature flexibility, volatility, odour, colour and compatibility. Recommended plasticisers include dioctyl phthalate, trioctyl phosphate and di-n-octyl phthalate, although many others may be used.

Polyvinyl Chloride pastes can be mixed with fillers and pigments in light blade-type mixers and paint roll mills whereas compositions for extrusion and calendering require expensive mixing rolls, Banbury mixers or other heavy duty mixers. It will be appreciated, therefore, that by use of pastes the manufacturer has readily available a cheap method of applying this plastic.

The preparation of P.V.C. pastes present few difficulties. The P.V.C. powder is mixed with plasticiser in a paddle stirrer. It is necessary to add stabiliser as in the case of ordinary compounding, and the same types are employed such as white lead, lead silicate, etc. The addition of colouring materials is very important and a wide range is available.

TABLE 127

TYPICAL PROPERTIES OF "WELVIC" PASTE

Property	Type of Paste		
	General Purpose Paste	Dipping Paste	Spreading Paste
(1) Viscosity . . .	70–110 Poises	6–11 Poises	350–450 Poises
Density at 25°C. . . .	1·26 (gm/c.c.)	1·24 (gm/c.c.)	1·27 (gm/c.c.)
(2) Tensile Strength (Gelled Sheet) . .	1,400 (p.s.i.)	650 (p.s.i.)	1,600 (p.s.i.)
(3) Volume Resistivity (Gelled Sheet) . .	2×10^9 (ohm/cm)	3×10^8 (ohm/cm)	5×10^9 (ohm/cm)
(4) Cold Bend (Gelled Sheet) .	—30° C.	—40° C.	—25° C.

An unlimited choice of colours varying from delicate pastel shades to very deep opaque types may be prepared. Colours used in ordinary P.V.C. compounding give good results in the pastes. Typical ones include anthraquinone and indanthrene blues, yellows and orange, phthalacyanine blues and greens, and the cadmium lythol reds.

Fillers may be added to the paste, and up to 25 parts on the paste give quite satisfactory results. The filler, which may be clay, silica, barytes, and so on, should be wetted out thoroughly with about 10 parts of added plasticiser. Pastes containing fillers tend to stiffen up fairly rapidly and should not be retained for any length of time as the shelf life decreases. As a general principle all pigments, fillers, etc., should be well ground with added plasticiser before incorporation into the paste.

Applications. The important applications of P.V.C. pastes which have already been developed include the coating of fabrics by spreading and dipping, the production of dipped articles, and the formation of mouldings. The coating of fabrics is a revolutionary development which has already attained major commercial importance. A very heavy coating can be applied at one operation. The coating may be up to 20 thousandths of an inch thick for example. Consequently the entire range of films can be made by this process including thin film for packaging, medium film for curtains, garments, etc., and heavy film intended for upholstery and leather applications. Where the films are applied on to fabric, it is particularly important that it is able to take up embossing with the greatest of ease.

Coating Methods. The equipment used for spreading P.V.C. paste on fabric, or for casting it, is similar to that employed in the rubber industry or in the artificial leather industry. However, no volatile material, no solvent, or water has to be removed.

In brief, the process consists of passing the fabric under a knife which is held at an adjustable height away from the fabric. The P.V.C. paste is held in front of the knife and a coating is carried through with the fabric. The thickness of the coating will depend on the height of the knife above the cloth, the type of fabric, and the speed at which the cloth is moving. The coated fabric has then to undergo the gelation process. Heat can be applied either by passing over steam-heated chests or over a steam-heated drum. Infra-red heating is also employed, being directed at the top surface of the material. A temperature of at least 150° C. must be attained. After the heating process the material is ready for collection or else it may be passed on to an embossing calender to receive its pattern. The time of heating will depend on the thickness of coating and the efficiency of the method used but it should not be more than a few minutes. Care must be taken not to tender any fabrics used.

Dipping and flow casting. There are two techniques commonly used for dipping:

(1) Cold forms are dipped into the paste, allowed to drain, heated, redipped and the process repeated until the desired thickness of film has been built up. Gelling is brought about by heat treating the coated forms at 140 to 150° C. for a few minutes. After cooling, articles are stripped from forms (an operation facilitated by dusting the form with chalk).

(2) Hot forms (90 to 110° C.) are dipped into paste which partially gels around the form. The thickness built up depends on the temperature of the form and length of time it is left in the paste. The usual practice is to remove the form after the correct period of treatment and to give it a final heating process at about 150° C. for a few minutes. After cooling, the article is removed as described above.

Flow casting and simple moulding processes. Hollow articles can be made by pouring the paste into a hot mould (90 to 110° C.) and then, after a given time, pouring off the excess paste. The paste gels on the walls of the mould and a final baking treatment at 140 to 150° C. is necessary to complete the gelation process. Mould is cooled before articles are removed.

Moulding can be carried out in several ways—compression and injection methods being applicable. Very little pressure is required to inject paste into moulds and a grease gun has been found to be very suitable for this purpose. After filling, the mould must be heated to 140 to 150° C. for a few minutes to complete the gelation process. The article is removed after the mould is cooled. One important advantage of this method of moulding is that very light and inexpensive moulds, made of plaster of Paris, brass or steel, can be employed.

Resin-Plasticiser-Diluent. P.V.C. paste formulations can be used with a diluent. The principal advantage of this system is that the diluent provides additional volume and retains fluidity during fabrication even with low plasticiser content. It is possible in this way to gain varying degrees of hardness in the finished product. Straight chain aliphatic solvents are recommended as diluents because they do not swell the resin, thereby maintaining low viscosity and increased storage life. The evaporation rate with this type of diluent is rapid enough so that none will remain after the resin has been fused. Small quantities of active solvents such as ketones and esters may be added to the mixture to stabilise the mix. These ingredients also help in the fusing process by softening the resin for the plasticiser.

Fairweather[10] has described a most interesting application of polyvinyl chloride to modify the properties of other materials, notably neoprene. Neoprene alone slowly absorbs oil, and polyvinyl chloride slowly loses in oils the plasticisers necessary to maintain its flexibility and firmness of shape. It is therefore proposed to obtain better results by using neoprene in conjunction with plasticised polyvinyl chloride. Simple mixing technique consists in plasticising the vinyl chloride, e.g. with tricresyl phosphate, and adding to the mass a preformed mixture of neoprene and vulcanising ingredients. A typical composition may be: polyvinyl chloride 100, powdered lead silicate 3½, tricresyl phosphate 75, with 30 parts of neoprene 100, litharge 20, rosin 5, magnesia 3, phenyl beta-naphthylamine 2, maleic acid 2. Such a composition is not appreciably affected by oils over prolonged periods.

The insolubility of polyvinyl chloride in solvents has an accompanying disadvantage, since it is difficult to stick P.V.C. No really satisfactory adhesive has yet been developed. Solvents such as cyclohexanone are effective with thin sheetings. The Germans have had some success with polyvinyl ethers, such as polyvinyl isobutyl ether.

Aqueous Dispersions of P.V.C. P.V.C. latex is available generally as an aqueous dispersion containing about 35 per cent solids. When dried above 70° C. continuous films are obtained. Below this temperature a friable powder is obtained. Film strength is attained by heating at 150° C. Plasticisers can be added in the form of emulsions.

One typical P.V.C. latex—Corvic—is a milky white fluid with viscosity of 2·5 to 4·0 centipoise at 25° C. Average particle size is less than 0·3 microns. Density is 1·1 and pH. is initially 11, dropping during storage.

The latex behaves in many ways like rubber latex. It can be concentrated by a creaming process. Fillers up to 30 per cent by weight, pigments and stabilisers may be added, first being wetted and thoroughly dispersed.

These dispersions are suitable for treating fabrics, yarns, paper and so on. For coating fabric the latex must be thickened by additions of about 3 per cent of methyl cellulose, casein, gelatine or algmates. A typical spreading compound is:

100 parts plasticised latex.

and a premix of

10 parts china clay.
1·2 parts white lead.
2·7 parts oleic acid.
3·3 parts 10% ammonia solution.

Latterly P.V.C. latex has been prepared which is already plasticised giving a flexible film when dried even without any application of heat.

Properties of Copolymers of Vinyl Chloride and Vinyl Acetate. An important series of resins is obtained by the copolymerisation of vinyl acetate and vinyl chloride. They are extremely versatile materials which lend themselves to fabrication by a very wide range of processes. A number of these copolymers have acquired commercial importance. According to the composition, the properties range from those of straight polyvinyl chloride on the one hand, insoluble in solvents, elastic, and difficult to work, to the relatively soluble, more rigid materials with the high proportions of vinyl acetate. Some indications of the versatility is shown by considering a few applications, which range from gramophone records, flexible tubings and sheetings, to coatings for cans and metals generally.

Efforts were made to use polyvinyl acetate to plasticise polyvinyl chloride, but physical mixtures were in every case found to be unsatisfactory. On the other hand, when the monomeric materials were polymerised together, there was a chemical combination with the formation of a polymer. In this, both vinyl acetate and vinyl chloride formed part of the same molecule chain. The ratio of the two materials can be varied over a wide range. From the point of view of rubber-like properties, these are only apparent when a very high proportion of vinyl chloride is present. In fact the leading product at the present time, (Vinylite VYNW) contains 95 per cent of vinyl chloride, being internally plasticised with the remaining 5 per cent of acetate. The product has a molecular weight of from 20,000 to 22,000.

According to Benedito,[2] current materials are:

	Vinyl chloride%	*Mol. wt.*
VYLF .	85–88	5,000
VYHH .	85–88	10,000
VYNS .	88–90·5	18,000
VYNW .	95	25,000
VYNU .	92–93	
VYNV .	98–99	

As the molecular weight and vinyl chloride content rise the resins become less soluble in organic solvents and progressively tougher. When plasticised, they are more elastic and have higher softening temperatures.

As the proportion of vinyl chloride decreases and vinyl acetate increases, so the copolymers formed become increasingly soluble in solvents. Thus materials where the ratio is 90 : 10 readily form solutions and are of interest in the coating field.

The series of resins available has a range of molecular weight from 6,000 up to 25,000. The lower ones at any given temperature are softer and more plastic; the high ones are harder, and have poorer flow.

These copolymer resins are colourless, tasteless, odourless, and non-toxic. They are extraordinarily versatile materials. Their compositions may be used by almost every technique. They are permanently thermoplastic but do not possess a true melting point, as they merely soften when heated. They will not support combustion. They are produced as a white, fluffy powder, making possible the production of transparent, translucent or opaque articles in the most delicate pastel shades. They are soluble only in ketones and related compounds, esters, chlorinated hydrocarbons, dioxane, propylene oxide, and mesityl oxide. They swell or dissolve in dichlorethyl ether, and in aromatic hydrocarbons.

They possess extreme chemical inertness, being unaffected by alkalis, oxidising agents, and most acids. Water, alcohol, and petroleum fractions have no action on them. Thus, in general, they share most of the properties of polyvinyl chloride.

They possess high internal plasticity, permitting the incorporation and use of a large number of different types of fillers and pigments when used in prefabricating operations. They are easier to compound or process than straight polyvinyl chloride. Smaller amounts of plasticiser are required and lower temperatures may be used. Although they darken on prolonged exposure to heat or direct sunlight, these properties may be improved by the use of small amounts, usually 1 or 2 per cent, of stabilisers such as lead stearate, lead oleate, calcium stearate, slaked lime, or somewhat larger proportions of the commonly used lead pigments. These stabilisers should be added to the powdered resin before fluxing on the mill or in an internal mixer. For use where flexibility of the product is a factor, the same range of plasticisers used with the straight polymer are likewise employed. The amount to be used is dependent upon the degree of flexibility required.

TABLE 128

PROPERTIES OF TYPICAL COPOLYMER COMPOSITIONS

	Type A	Type B	Type C
Tensile strength, lb. per sq. in.	2,500	2,000	1,300
Elongation, per cent	300	330	350
Low temperature flexibility, °C.	−17	−30	−39
Tear resistance, lb. per in.	30	25	20
Hardness (Shore)	86	75	67
Fatigue resistance, cycles to failure	500,000	>1,000,000	>1,000,000
Abrasion loss, vol. in proportion to rubber as 100	80	70	62
Specific gravity	1·23	1·20	1·18

These materials are very resistant to water, soapy water, dilute acids and dilute alkalis, but stiffen when immersed in alcohol, petrol and oil. Other compositions have improved resistance to alcohol, petrol and oil. These are non-inflammable.

General Resistance of Copolymers. Copolymer resins have outstanding resistance towards corrosive agents and solvents. Higher molecular weight resins are in general more resistant, especially to organic solvents, than the lower molecular weight resins. The presence of other materials such as pigment, wax, stabiliser, etc., in filled compounds or coatings also may alter the behaviour.

The properties of these copolymer plastics vary widely, depending on the grade of resin used, the type and amount of plasticiser, fillers, and other ingredients which may be incorporated. The grade of copolymer will be dependent on the relative proportions of vinyl chloride and vinyl acetate present in the molecule, and the degree of polymerisation.

The rubber-like properties are brought out by the addition of plasticisers, similar materials as used with the straight polymer, e.g. tricresyl phosphate, dibutyl phthalate, but a rather wider range is effective in this case than with polyvinyl chloride.

Compounding and Fabricating. The temperature range in which both polymer and copolymer can be handled is more critical than with rubber compounds, and it must be controlled more accurately throughout the compounding and fabricating processes, as the characteristics and the quality of the final product, as well as its ease of fabrication, are thus influenced.

The actual compounding is done first by blending all of the dry ingredients and preferably the lubricant and plasticiser without heat before feeding to the Banbury mixer. This assures that all of the resin comes in contact with the stabiliser before it is fluxed or heated.

Overheating must be avoided. Mechanical working of large masses generates considerable internal heat, which, if excessive, may bring about undesirable physical and chemical changes in the resin. Even moderate overheating causes a certain loss of plasticity with consequent difficulty in fabricating. Further overheating may cause decomposition with liberation of traces of hydrochloric acid. For the same reason care must be exercised to avoid storing the stock hot for long periods of time.

The same precautions are necessary when transferring the material from the mill to the calender or extruder. Calendering is done with heated rolls with the stock at a temperature of 120° C. to 130° C. The sheeted stock can be cooled either in air or by immersion in water.

The same defects as are found in the polyvinyl chloride, also exist here. The material is rather more heat-stable than polyvinyl chloride, although it is sensitive to traces of iron and zinc which tend to make it decompose.

Elastic Compositions based on Polyvinyl Chloride-Acetate. Plasticised vinyl chloride-acetate copolymer has considerable flexibility, is resilient, and in many respects resembles rubber. Such compositions are resistant to many of those factors which cause rubber to deteriorate, such as oxygen, ozone, sunlight, in the presence of metallic salts, etc. They have other features such as unlimited colour range and transparency, which are not attainable with rubber. Although they are prepared along similar lines and with similar equipment as used with rubber, yet they do not require to be vulcanised, consequently production is greatly accelerated. Plasticised material is available in a number of forms. Sheets and films are available in all colours, either transparent or opaque, in continuous rolls of varying thicknesses. The materials can be fabricated with everyday equipment. They can be bonded by the use of cements, they can be sealed by heat, or they may be sewn. Other compositions are employed for application to cloth by means of the calender. Other forms are extruded into rods, tubes, and articles of varying cross sections. The copolymer plastics are extensively used for covering wires and cables.

Apart from these applications they may be moulded either by compression or injection to give a wide variety of products. Among moulded articles of great interest are such things as gramophone records, and tiles. It is advisable to chromium plate moulds, dies, extruders, etc., or otherwise protect the copolymer from contact with hot iron or steel which attacks it.

Outstanding Characteristics of Elastic Compositions. Vinyl chloride acetate plastics have excellent resistance to oxygen and ozone. They are unaffected by these agents at ordinary temperatures. They withstand prolonged exposure to sunlight without any marked alteration in physical or electrical characteristics. If properly compounded and plasticised, the materials will not deteriorate over very long periods, even in hot, humid climatic conditions.

The toughness and abrasion resistance are outstanding properties of these materials. The tensile strength is as high as that obtained from high grade rubber compositions. Specially designed types have abrasion resistance which is superior to that of rubber compounds.

The copolymer plastics are quite non-inflammable and will not support combustion. They are superior to rubber in their ability to withstand the effect of water, oils, and solvents. When properly compounded the materials are also resistant to many acids and alkalis. The elastic behaviour of the flexible materials is impressive. Sheets have been made which could withstand three million flexing cycles under test without cracking. The behaviour under extension is of great interest. Suitable compositions can be stretched to 500 per cent of the original length. The elastic recovery is much slower than in the case of rubber; it lacks the snap. However, recovery is almost complete and the slow recovery is of use for damping vibration.

While copolymer compositions crack more readily than rubber at low temperature, suitable compounding enables very low crack points to be attained, e.g. of the order of $-50°$C.

The electrical characteristics of these materials are quite good, both when wet and dry. They show high dielectric strength at ordinary temperatures of the order of 1,000 volts per mil on thin sheets. Dielectric constant at one megacycle per second is of the order of 9 at 70° C.

These plastics can be pigmented to give any colour requirement.

Depending on the nature of the pigment they remain stable at exposure to light and to reasonable temperature.

The copolymer has had a very wide application. It can be prepared as a highly polished transparent sheet, glass clear, or in any colour. It is used for many articles of attire such as belts, garters, and suspenders, shoe fabrics, raincoats, and so on. It has also been fabricated into such things as umbrellas, handbags, tobacco pouches, trunks, flooring, and numerous other diverse articles. It is employed for the coating of fabrics and so on. Artificial leather is made by applying tough flexible composition of vinyl chloride-acetate copolymer on to a sturdy fabric backing by means of a calender. Thereafter it can be embossed or given any desired surface grain effect, etc. Such products are likely to have a big future for upholstery. One outstanding use in the United States has been the coating of binoculars.

Fig. 193. Use of extruded strips and threads of vinyl copolymer material

Applications. Copolymers have found uses similar to those developed for straight P.V.C. Cloth is coated with these plastics on a very large scale. Thinner coatings than with rubber are found to give satisfactory service, so that light-weight proofings are extensively made. Raincoats, tarpaulins, and floating equipment are outstanding examples of current applications.

By comparison with rubber these coatings do not tend to become sticky in hot climatic conditions. They are moisture-proof; and they are free from odour under all conditions.

Cloth coated with heavy coatings of these elastic materials are used for heavy service, such as upholstery applications in aircraft, tanks, and ships. They are found to have all the necessary characteristics for hard usage.

The plasticised copolymers are widely used for covering wires and cables. In this respect the copolymers share the field with straight polyvinyl chloride plastics. They have the advantage over rubber of being non-inflammable, resistant to abrasion, and resistant to corrosion.

Extruded tubing is also exclusively used for hose of various descriptions to handle water, oil, petrol, etc. There are many other applications in the extruded form.

Moulding Technique. These materials are well suited for moulding, either by compression or by injection. For compression moulding steel moulds, or preferably chromium plated moulds may be employed. Pressures range from ½ ton to 1 ton per sq. inch. Temperatures range from 110°C. up to 170°C. depending on the composition. All articles must be cooled under pressure before removal. This affords a very useful method for making flexible articles. Compression moulded articles include gramophone records and accumulator components. A whole range of small articles are made by injection moulding for use in many forms of water equipment.

In the extruded form the use for covering wires and cables takes pride of place. It is also extruded as tubings of every type.

The Production of Vinyon Thread. It is utilised as thread in fabrics (e.g. *Vinyon*), for industrial purposes and as tape and strip for a variety of uses. The type of copolymer used for these applications is made up of 89 per cent vinyl chloride, and 11 per cent vinyl acetate.

This degree of copolymerisation is interesting in that the vinyl acetate seems adequately to plasticise the vinyl chloride internally, and no other plasticiser is necessary.

The copolymer resin, as a white fluffy powder, is dissolved in acetone to get a rather heavy, viscous spinning dope containing about 25 per cent by weight of the resin in solution. This is filtered, de-aerated, and spun downwards in air through multiholed stainless-steel jets, just as is done in acetate spinning, the solvent acetone being removed by a current of warm air and recovered. After being conditioned on the take-up bobbin the yarn is stretched either directly or after being plied with one or more ends. The method resembles that used for making cellulose acetate yarn, etc. They have the appearance of long transparent skeins like knitting yarn. The yarn is set by heating, while under tension, to about 90° C.–100° C. This treatment makes the yarn stable to shrinkage up to at least 65° C., but when heated above this temperature shrinkage of the yarn occurs with a corresponding reduction in tenacity and increase in elongation. Mineral acids do not attack "Vinyon" at room temperature, even in high concentrations; it is also unaffected by water; in fact, it may be considered water-repellent, although its surface can be wetted by using some of the commercial wetting agents. Small amounts of "Vinyon" staple have been successfully used in making cotton, wool, and glass felts; the thermoplastic resin functions as a binder, which not only gives added strength, but shortens the time of manufacture. Its largest use at the present time is in the manufacture of industrial filter cloth, because of its unusual properties. Other suggested uses are for shower curtains, bathing suits, waterproof acid and alkali-resisting clothing, fully-fashioned hosiery, fireproof awnings, etc. Material having a diameter of 0·07 m/m. has been used for hat trimmings and synthetic jewellery, etc. These yarns can be braided, knitted, or crocheted.

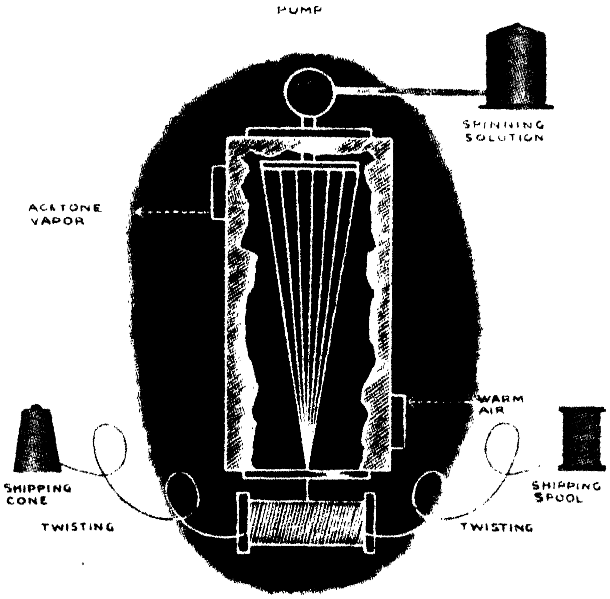


Fig. 194. Production of fibres from solutions of plastics

The latest development in this field is Vinyon N.[18] This is a copolymer of vinyl chloride and acrylonitrile made specially for fibres. The fibres have high-strength, toughness, and chemical resistance. They have a negligible water take-up. They are not inflammable and mildew resisting. The best strength is developed by stretching to 1,000 per cent at 120° C.[23]

Most polyvinyl chloride and high chloride content polymers are being used for insulation purposes at the present time both in Britain and in the United States. The lower chloride-containing copolymers such as VYHH, are being used for proofings and general coating production. In particular they are being used to line food containers, tins, and cans. They are also widely used for coating metals against chemical corrosion.

Chlorinated Polyvinyl Chloride.[30] The Germans have made considerable progress in the after-chlorination of P.V.C. The main object was to produce a material which could be taken up in suitable solvents.

The procedure is to place tetrachlorethane in a porcelain-tiled mild steel tank. The temperature is taken up to 90° C. and P.V.C. is added up to 10 per cent of the weight of tetrachlorethane. The temperature is brought to 60° C. and chlorine passed in. The temperature is allowed to rise slowly, reaching 115° C. at the end. Test samples are run off and tested for solubility in acetone. Hydrogen chlorine is taken up in chalk towers. The cycle takes 23 hours and the final product contains 64 per cent chlorine. It is soluble in acetone.

The chlorinated P.V.C. is precipitated in brine cooled porcelain-lined tanks by addition of methanol. The precipitate is filtered at 0° C. and vacuum-dried at 50° to 60° C., taking 24 hours. The main use of the white powder is for PeCe fibres and lacquers.

The *PeCe* fibres are directly derived from polyvinyl chloride. They are actually made from chlorinated polyvinyl chloride. They were developed by the I.G. Farbenindustrie. The outstanding feature of this material is the unsurpassed resistance to acids, alkalis, and oxidising and reducing media. Even aqua regia and 50 per cent caustic soda solution, which completely decompose wool and cotton in a few minutes, are without effect after 24 hours. In addition, the synthetic fibres are not affected by the long-term action of water: they neither swell nor develop mildew. Their electrical insulating properties are better than those of silk. Finally, they are wholly uninflammable; if brought into direct contact with a flame they simply melt, but solidify again when the flame is removed. The only significant disadvantage of the fibres for purely textile use is that the low softening point of 85°–90° C. of the fibres does not allow textiles made from them to be boiled or ironed in the usual way.

All these properties lead to a variety of preferred uses for such fabrics, of which the most important are the following: filter media in the chemical industry; protective coverings, belts, and cords in acid processes; insulating materials; and fishing-nets for fresh water.

The life of filter cloths made from this fibre has been shown to be on the average five or six times as high as that of cotton or woollen clothes. In some cases they have been found to last thirty or fifty times as long. Protective coverings used in acid and alkaline processes have lasted a year or more in uses in which woollen coverings of double the thickness have collapsed after three or four months' use. A special feature of the employment of these textiles in acid baths and the like is that, unlike hemp, etc., they do not become tender. Further uses of special importance for acid processes are for float cords in acid tanks, switch cords for lamps, and so on; while packing glands have proved of greater value than asbestos in operations with 96 per cent sulphuric acid and 20 and 65 per cent oleum.

The resistance of the polyvinyl chloride fibre to the action of water and to rotting make it of great value in marine operations of all kinds, especially as compared with linen in biologically active waters. For example, cotton fishing-nets, even when regularly impregnated with preservative materials, were found to last one or at the most two years under certain severe conditions, while polyvinyl chloride nets were still in use after four years and showed no sign of decay. The advantage of these fibres in this connection lies not only in their longer life, but also in that they require no special attention such as the application of preservatives.

Other copolymers of present-day significance include those made in the U.S.A. with vinyl chloride and vinylidene chloride e.g. Geon 200.

		K-value
Igelit in P. Grade A.	80 vinyl chloride 10 ethyl maleate 10 methyl maleate	55–60
Igelit in P. Grade K. (for wire covering)	84 vinyl chloride 16 methyl acrylate	72
Igelit in P. Grade A K. (unplasticised for moulding)	80 Vinyl chloride 10 methyl acrylate	70
Igelit in P. Grade D.	80 vinyl chloride 20 methyl acrylate	

Vinylidene Chloride Polymers. Vinylidene chloride (1, 1—dichloroethylene) was first found by Regnault in 1839.

Bauman in 1872 described the formation of a white substance when dichloroethylene was exposed to sunlight. Ostromislensky found that vinylidene chloride polymerised in light to a white amorphous mass insoluble in many solvents. Chief production work has been carried out by the Dow Company in the United States and the I.G. Farbenindustrie in Germany. The first commercial products appeared in the U.S. in 1940.[8] Only small quantities have been available in this country so that work carried out here has been somewhat limited. However, there has been opportunity to consider the characteristics and possibilities of the materials.

Monomer Preparations. Vinylidene chloride ($CH_2{=}C.Cl_2$) can readily be prepared from 1.1.2-trichloroethane by removal of one mol. HCl either by thermal dehydrochlorination at elevated temperatures (300°—500°) or by liquid phase treatment with alkali or alkaline earth hydroxides, the latter being a most convenient method.

The raw material, 1.1.2-trichloroethane, can be produced by chlorination of vinyl chloride in the gas phase or better in the liquid phase in presence of a diluent, preferably trichloroethane itself. Vinylidene chloride can also be obtained by high temperature chlorination of ethane in which process both steps, the chlorination to trichloroethane and the thermal dehydrochlorination would seem to proceed simultaneously. Whatever the route by which vinylidene chloride is prepared, the raw materials are chlorine and a C_2-hydrocarbon.

Monomeric vinylidene chloride, a colourless liquid boiling at 31·7°/760 mm., $d_4^{20} = 1{\cdot}2129$ and $n_D^{20} = 1{\cdot}4249$, decomposes when exposed to air and light with evolution of HCl, phosgene and formaldehyde, simultaneously depositing some polymer as whitish powder.

If vinylidene chloride is to be used for polymerisation, its storage in absence of air or oxygen and light is essential. For prolonged storage it is advisable to add inhibitors such as pyrogallol, phenyl α-naphthylamine, pyridine or quinoline and to remove these by washing or distillation (in absence of air) immediately before polymerisation.

Vinylidene chloride polymerises readily at temperatures above 0°C. to form a polymer which is insoluble in the monomer and precipitates as a white powder. It is completely saturated. Its structure is considered to be a straight chain linear polymer consisting of up to 1,000 monomer units.

Polyvinylidene chloride is a white porous powder with a softening range of 185°–200°C. and a decomposition temperature of about 225° C.

The utilisation of the straight polymer is difficult because of:

(*a*) Its high softening range,
(*b*) Its tendency to evolve hydrogen chloride at working temperatures,
(*c*) Its incompatibility with usual plasticisers.

The difficulty has been overcome by copolymerisation. Vinylidene chloride forms copolymers with many vinyl compounds, notably with vinyl chloride.

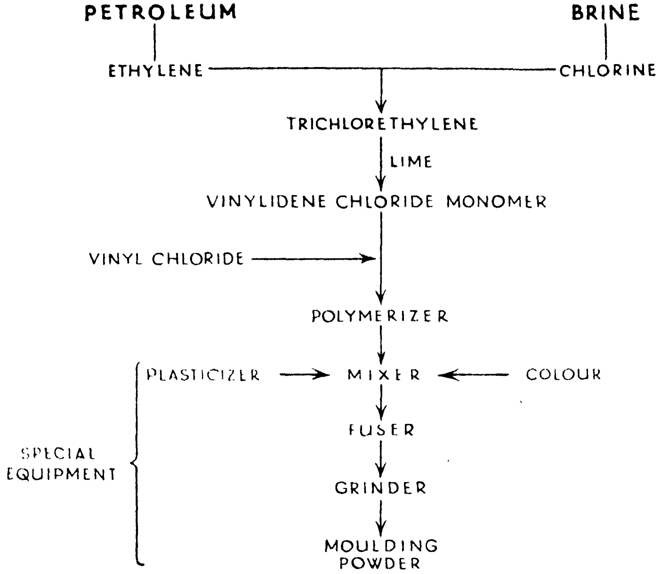


Fig. 195. Flow sheet for polyvinylidene chloride

By selection of copolymers and control of the polymerisation conditions, polymers can be formed which have softening points ranging from about 70° to at least 180° C. Soft flexible materials and hard rigid materials can be obtained. According to Goggin and Lowry[12] present commercial polymers have softening points from about 120°C. to 140°C., with a molecular weight of approximately 20,000. These polyvinylidene chloride plastics are known by the trade name "*Saran.*" They are available as powders or granules already coloured and plasticised. They are made by ball-milling the ingredients.

The copolymers are obtained as white powders which have no odour or taste, and are non-toxic. They are very tough and have high abrasion resistance.

The behaviour of polyvinylidene chloride and its copolymers is dominated by the fact that it is a crystalline material. As such it has a fairly sharp melting point. It shares this property with the other crystalline plastics, nylon and polythene.

The crystallisation is most marked in the straight polymer and decreases in the copolymers. Crystallinity of polyvinylidene chloride was discovered by Feisst.[11] It is shown by definite X-ray diffraction patterns (amorphous materials do not give a pattern). When melted polyvinylidene chloride becomes amorphous. On standing it tends to revert to the crystalline condition. Stretching causes orientation.

Goggin and Lowry have summarised these facts as follows:

1. *Crystalline.* The normal "as-polymerised" state, giving a sharply defined X-ray pattern, but also known to be partly amorphous. It is hard and tough, resembling ordinary plastic materials.

2. *Amorphous.* Soft, easily deformed material obtained by fusing and rapidly cooling crystalline polymer; reverts to the crystalline form under suitable conditions. It is soft and rubbery.

3. *Oriented Crystalline.* Tough, strong and very flexible showing characteristic X-ray fibre pattern; produced by plastically deforming either partly crystalline or amorphous material.

Properties of Polyvinylidene Chloride. Polyvinylidene chloride is extremely resistant against chemicals and solvents. At room temperature it withstands to all acids and all common alkalis, except for concentrated ammonium hydroxide. Slight discoloration with little change in mechanical properties will occur when exposed to concentrated sulphuric acid or sodium hydroxide over long periods. It is substantially unaffected by both aliphatic and aromatic hydrocarbons, alcohols, esters, ketones, and nitroparaffins. It is swelled or softened only by oxygen-bearing organic solvents such as cyclohexanone and dioxane. The resistance to chemicals or solvents decreases with rise in temperature. The resistance of saran to any chemical is in part a function of the crystallinity of the polymer. It is chemically more resistant in the crystallised form than in the amorphous state.

Polyvinylidene chloride has very low water absorption and vapour transmission. Over long periods of immersion, it shows no water absorption. This behaviour is only equalled by polystyrene. This low value accounts for its dimensional stability and freedom from warpage under a wide range of moisture-exposure conditions. Resistance to moisture transmission is at least five times that of the best commercially available organic film.

The control of extrusion and subsequent heat treatment of saran permits a range of properties to be obtained. Tensile strengths can thus be controlled from 4,000 to 12,000 pounds per sq. inch, hardness from 60 to 95, elastic elongations from 10 to 40 per cent. Such products have good fatigue life as illustrated by the following example:

Specimens of $\frac{5}{16}$-inch tubing having a wall thickness of $\frac{1}{16}$-inch are unruptured when flexed through a 15° arc 1,750 times per minute for 2,500,000 cycles. In comparison, standard $\frac{1}{4}$-inch copper tubing failed after about 500 cycles in the same test.

The copolymers now available require special technique in their fabrication. When hot they are catalytically decomposed by iron or copper. These must be avoided in equipment while stabilisers must be added as in the case of polyvinyl chloride.

The outstanding uses of saran so far have been by extrusion, in order to take advantage of the orientation properties. Screw-type extrusion machines have been modified to permit streamline plastic flow and uniform heating, together with the use of new types of stretching and winding machinery. Cordage (0·010–0·100 inch diameter filaments) and tubing have gained industrial prominence, and intensive work on textile fibres is continuing. Firestone make the type known as Velon.[22]

Polyvinylidene chloride copolymers are being injection moulded in special equipment. The use of cold dies results in supercooled articles suitable for further treatment. Oddly enough hot dies are employed. Heated dies permit crystallisation, desirable for rapid cycles and dimensional accuracy of the finished piece. In crystallising it becomes rubbery and may be ejected hot. Very rapid moulding cycles are permitted.

The combination of thermoplasticity with crystallinity allows these materials to be fabricated by cold or hot rolling, forging, blowing, stamping, and welding.

Only a few plasticisers (not the common types) have any influence with polyvinylidene chloride. Lead compounds exert a stabilising effect. Plasticised and stabilised copolymer compositions are available as moulding powder or in fabricated shapes under the name of saran.

Applications of Saran. Because of its unusual combination of chemical inertness, strength, and toughness, saran promises to become a plastic of major importance. Extruded and oriented saran has been used in heavy textiles, ropes, braids, belts, and upholstery fabrics. It is outstanding as filter cloth. Extruded Saran tubing, rods, and other structural shapes are employed as process piping for a variety of mechanical parts. They are playing an important part in replacing metals in short supply. Injection and compression mouldings of Saran have solved difficult moulding and application problems where its superior mechanical and chemical properties are essential. For example, it is widely used as mouldings for the rayon industry because it withstands the chemicals concerned.

The crystal orientation of polyvinylidene chloride is of outstanding interest and merits fairly close consideration. In some ways the technique resembles that employed with nylon. The oriented form is produced by extrusion, subsequent plastic deformation (as by stretching), and heat treatment. It is thus possible to obtain long, continuous extrusions of monofilaments, tapes and other shapes which have exceptional properties.

TABLE 129

RANGE OF PHYSICAL PROPERTIES OF SARAN RESINS

Specific gravity		1·6–1·75
Refractive index	N_d	1·60–1·63
Tensile gravity	lb. per inch^2	Up to 60,000
Elongation	%	25
Modulus of elasticity	lb. per inch$^2 \times 10^5$	0·4 × 2·4
Flexural strength	lb. per inch^2	15,000–17,000
Thermal conductivity	10^4 cal. per sec. per sq. cm./°C. per cm.	2·2
Specific heat cal. per	°C. per gm.	0·32
Resistance to heat	°C. (continuous)	70°–95°
Softening point	°C.	95°–160°
Distortion under heat	°C.	68°–95°
Tendency to cold flow		Slight
Volume resistivity	ohm-cms. (50% relative humidity and 25°C.)	6×10^{13}
Breakdown voltage	60 cycles volts/mil. (instantaneous)	500–2,500
Dielectric constant	60 cycles	3·0–5·0
,, ,,	10^3 cycles	3·0–5·0
,, ,,	10^6 cycles	3·0–5·0
Power factor	60 cycles	0·03–0·08
,, ,,	10^3 cycles	0·03–0·15
,, ,,	10^6 cycles	0·03–0·05
Water absorption	Immersion—24 hrs.	0·00
Burning rate		None
Effect of age		Becomes stronger
,, ,, weak acids		None
,, ,, strong acids		None
,, ,, weak alkalis		None
,, ,, sunlight		Slight
,, ,, organic solvents		Highly resistant
,, ,, strong alkalis		None
,, on metal inserts		Inert

When the technique employed for fabricated polyvinylidene chloride is studied, it becomes apparent that in many ways they are similar to methods in use in handling metals except that the temperature range is lower. Thus according to Goggin and Lowry:

"In the production of strong, continuous sections, the plastic must be uniformly heated to a temperature above its crystallite melting point and thereafter cooled below this point. Preferably the material is mechanically formed to a shape similar to that of the section desired before being cooled. One method of fusing and shaping involves the use of a screw-type extrusion machine. The degree of cooling may be sufficient to reduce the temperature of the fused, shaped mass to about room temperature. The material will remain in this amorphous or supercooled condition for a sufficient time to permit cold-working operations to be carried out. The saran is now ready for the orientation step.

"The orientation process provides a method of effecting plastic deformation and partial recrystallisation of the shaped, supercooled material. It involves an accurately controlled, predetermined rate of withdrawal of the plastic from the extrusion unit. The ultimate size and uniformity of the continuous section is governed by controlling the withdrawal rate.

"The shaped, supercooled material is then elongated under controlled conditions, preferably at room temperature. During this mechanical stretching, there is a partial recrystallisation of the material and orientation of the crystallites along the major axis of the strand. The reduction in cross-sectional area is approximately proportional to the elongation which takes place. The material may be heat-treated after or during stretching to affect the degree of crystallisation and thus control the properties of the oriented article.

"The above method will produce orientation in a single direction with resulting unidirectional properties. The resulting tensile strength is a function of the elongation. These unidirectional properties of high tensile strength, great flexibility, long fatigue life, and good elasticity are particularly desirable for small monofilament sections where the load is along the longitudinal axis. In larger, non-circular section, such as tapes, ovals, and semicircles, the desired degree of transverse orientation can be realised and accompanying transverse properties controlled through the introduction of other factors in the continuous process. For example, a rolling operation incorporated after the quenching step produces some flattening and transverse elongation of the strand with a resultant increase in transverse strength."

Water Dispersion of Saran for Coating Purposes. Saran has latterly become available as latices which are colloidal dispersions of solid polymer in water. The particle size, observed with an R.C.A. type B electron microscope, is uniform and ranges from approximately 0·08 to 0·15 micron. The solids content can be made as high as 60 per cent, without sacrifice of particle size or distribution. The latices are somewhat sensitive to coagulation by electrolytes and water-miscible liquids. Infinite dilution of the latex with hard water produces no coagulation or unstabilising effects.

In common with other water dispersions, the saran latices show greater stability in contact with certain metals than with others. The order of preference of representative metals found to be satisfactory for processing and handling of the latices with the pH adjusted between 5 and 8, are as follows: stainless steel, chromium, tin, bronze, brass, nickel, aluminium. The pH of the latex as normally furnished is in the range of 6·5 to 7·5, which may be raised to 12 by addition of ammonia, although some discoloration may occur in the higher range. Coagulation begins at a pH below 2.

The viscosity of the latex usually marketed is approximately 22 centipoises at 57 per cent solids. This can be raised to any desired viscosity by the addition of small amounts of available thickeners, typical examples being hydroxyethylcellulose and sodium or ammonium alginate. Some degree of thixotropy is encountered as the viscosity is increased by addition of thickener.

A variety of plasticisers have been found suitable, either singly or in combination, for use with the saran latices, including organic esters of phthalic, glycolic, sebacic, and phosphoric acids. Water-soluble materials, such as dyes, lubricants, corrosion inhibitors, etc., may be added as water solutions or stirred directly into the latex. Water-insoluble extenders and modifiers, such as pigments, fillers, clays, etc., can best be incorporated in the form of water slurries or pastes.

A typical formulation for a coating composition to deposit a colourless, glossy, transparent, flexible finish on paper, cloth, wood, etc., comprises 100 parts saran latex (57 per cent solids), 23·8 parts dibutyl phthalate emulsions (60 per cent dibutyl phthalate), and 1·7 parts hydroxyethylcellulose solution (5 per cent solids).

REFERENCES

1 BARRON, DEAN AND SCOTT. *Trans. I.E.E.*, 1944, **91**, 297.
2 BENEDITO. *British Plastics*, 1943, **15**, 175.
3 BAUMANN. Ann. 1872, **163**, 308.
4 BROUS. U.S.P. 2,234,621/1930.
5 BROUS AND SEMON. *Ind. Eng. Chem.*, 1935, **27**, 667.
6 BUCHMANN. *Kunstoffe*, 1940, **30**, 357.
7 Carbon and Carbide Corporation. U.S.P. 1,755,882/1930; U.S.P. 2,161,766/1939.
8 Dow Chemical Co. U.S.P. 2,160,903/1939.
9 Du Pont de Nemours. B.P. 319,887/1928.
10 FAIRWEATHER. B.P. 539,834/1941.

11 FEISST. *Helv. Chim. Acta*, 1930, **13**, 832.
12 GOGGIN AND LOWRY. *Ind. Eng. Chem.*, 1943, **35**, 422.
13 I.G. Farbenindustrie. B.P. 500,298/1939; G.P. 362,366.
14 LAWSON. U.S.P. 1,867,014/1932.
15 OSTROMISLENSKY. *Chem. Ztg.*, 1912, **36**, 199; *Caoutchouc and its Analogues*, Moscow, 1913; *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 114; U.S.P. 1,721,034/1929.
16 QUATTLEBAUM AND NOFFLINGER. B.P. 557,477/1943.
17 REGNAULT. *Ann. Chem. Phys.*, 1838, **65**, 157.
18 RUGELEY, FIELD & FREMON. *Ind. Eng. Chem.* 1948, **40**, 1724.
19 Saran. Dow Chemical Corp. Technical Literature.
20 SCHOENFELD, BROWNE AND BROUS. *Ind. Eng. Chem.*, 1939, **31**, 964.
21 SEMON. U.S.P. 1,929,453/1933; B.P. 398,091/1933.
22 Velon. Trade mark of Firestone Corporation.
23 Vinyon N. *Chem. Eng.*, 1948, **55**, 120.
24 Welvic Paste. Imperial Chemical Industries Ltd. Technical Literature.
25 WICK AND ILOFF. *Kunstoffe*, 1942, **32**, 137.
26 Photographs by courtesy of Imperial Chemical Industries, Ltd.
27 ,, ,, Francis Shaw, Ltd.
28 C.I.O.S. XXXIII–23, p. 22.
29 C.I.O.S. XXVIII–13.
30 B.I.O.S. 104.

CHAPTER XXII

PLASTICISERS AND THEIR APPLICATIONS

MOST synthetic resins or cellulose derivatives exist as white powders, or as horny tough products. In these forms the plastic characteristics are latent, and the degree of flow under heat and pressure is comparatively limited, so that these raw materials cannot easily be processed.

As a result, applications of the "straight" materials are relatively few and thermoplastic materials are comparatively rarely used without some modifying ingredient. Notable examples which are used alone include polystyrene, polythene, some acrylic polymers and nylon, but the many others, including cellulose plastics, polyvinyl materials, and so on, must invariably be modified to have any wide commercial usage. In general, they must be plasticised by the incorporation of plasticisers, which are generally liquids of high boiling point.

The addition of plasticisers brings out the best characteristics of most synthetic resins, and, in fact, makes them into workable plastics. The lack of suitable plasticisers is a handicap and, in some cases, has held up development. A typical example is cellulose acetate, where the requirements have only latterly been solved. In the case of polystyrene, no really satisfactory plasticiser has yet been evolved, so that, although it is used alone, it has disadvantages.

Plasticisers Improve Processing of Plastics. When cellulose derivatives or vinyl derivatives, etc., are used in manufacture by processes such as moulding, or casting, or extrusion, or as lacquers, a suitable plasticiser must be added. Thus additions of more than 20 per cent plasticiser are necessary with cellulose acetate. Even larger amounts are required for polyvinyl chloride. The plasticiser becomes an integral part of the plastic material, and, suitably mixed, the resins will give coherent plastic masses. Previously brittle materials will have acquired elasticity, flexibility, strength and toughness.

Where moulded articles are being made, the addition of a plasticiser enhances the flow of the plastic under heat and pressure. Where articles are being extruded, the plasticiser also assists the flowing characteristics during the extruding operation. If used in films or coatings, plasticiser enhances the flexibility. They may also improve water resistance and other characteristics. Actually, extensibility is the property most affected by addition of a plasticiser. The related characteristics of strength, flexibility and toughness are also affected.

Characteristics of Plasticisers. Most plasticisers are liquids, a few solid. They have been described as "non-volatile solvents," and have the essential characteristics of high boiling points and low volatility.[2] These factors are fundamental because, if the plasticiser evaporates from the plastic or film, then these will revert to the brittle condition. This is frequently evident in poorly compounded materials, and is a leading source of criticism of plastics. In consequence, the boiling point of plasticisers in general should be higher than 300°C. The softening plasticising effect of these materials is their fundamental characteristics, but there are many other properties also conferred on the plastic. As already stated, plasticisers lower the resistance of the plastic to flow under the moulding pressure, but they also lower the temperature needed to give adequate flow at a given moulding pressure.

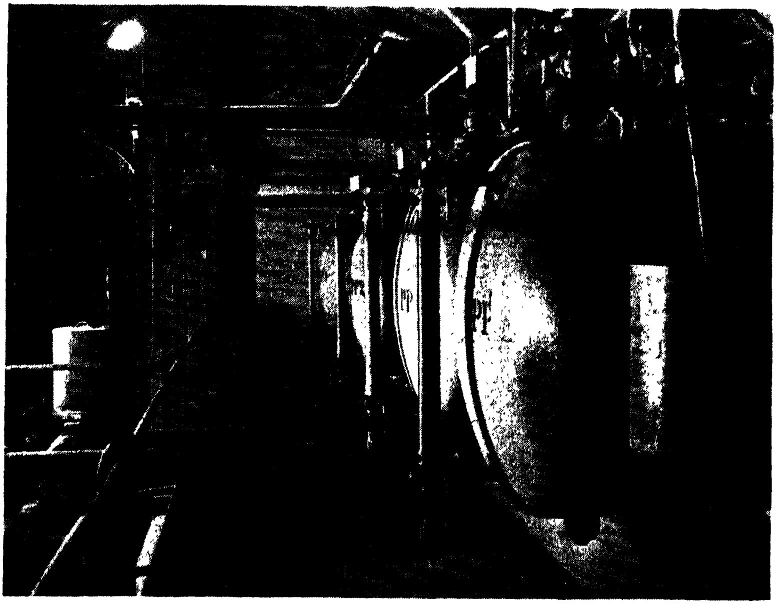


Fig. 196. Storage tanks for plasticisers for polyvinyl chloride

The general properties of the plasticiser must conform with the requirements of the article ultimately to be produced. In general, it can be readily seen that plasticisers must be chemically inert, fast to light, and resistant to moisture. From the angle of production and handling, they should be non-toxic, non-fuming, etc. If the produce is to be used for food or beverages, these factors become even more critical. There must be no smell or taste.

There are, however, a few basic qualities which seem necessary in all good plasticisers. The compound should: (1) be compatible with the polymer, (2) impart flexibility, (3) show permanent retention, (4) be water insoluble, and (5) be stable in the presence of water.

The chemical composition of the plasticiser has a very profound influence on the behaviour. Plasticisers based on phosphates are generally non-inflammable and impart this characteristic to plastics. Hydrocarbon plasticisers have good electrical properties, and, where possible, are used for insulating materials. Other plasticisers, such as oils, improve the moisture resistance.

So far as the physical characteristics are concerned, the most important perhaps is the solubility in the medium. This gives a measure of the affinity existing between materials and plasticiser; this affinity may, indeed, outweigh other disadvantages, such as high volatility and low boiling point.

Where good solvent action is a feature, then the resulting plastic is extremely tough, but has a tendency for cold flow. Where there is little solubility, high tensile strength is obtained, the products are more rigid and are less resistant to impact.

Retention of plasticiser is of the utmost importance. Rapid loss of large quantities of plasticiser, i.e. ageing under service conditions, is the primary cause of complaint in the use of plastics generally. In such cases moulded articles tend to warp or buckle, sheets such as are used in laminated glass may shrink, insulation loses flexibility, polished surfaces become dull, and so on.

The general characteristics of plasticisers which are of interest are melting point, boiling point, specific gravity, refractive index, and so on. Mellan[8] has listed no fewer than 23 criteria. The type of application will influence the relative importance of these properties.

The Important Plasticisers. The leading commercial plasticisers used for preparing plastics fall into several chemical groups; for example, phthalates, aryl phosphates, sulphonamides, glycollates, chlorinated hydrocarbons, etc.

From the angle of quantity the phthalate plasticisers are used on the largest scale. In fact, demands for phthalic anhydride and derivatives have caused some embarrassment owing to war conditions. The number of plasticisers is legion. New types are always being prepared, but only a few are used on any large scale. The following brief accounts describe some of the leading materials in everyday use.

Tricresyl Phosphate. Tricresyl phosphate is a colourless liquid having a specific gravity of 1·175 at 20°C. It has a very high boiling point and very low volatility. The loss on evaporation after heating for 100 hours at 100°C. is only ·2 per cent. It freezes at −35°C. It mixes freely with all the common solvents, with oils such as castor oil, linseed oil, tung oil, etc. It has low solubility in water, and in general imparts good moisture-resisting characteristics.

It is one of the widest-used plasticisers, being employed for almost every type of plastic and lacquer. Almost the only leading plastic where it is not of any particular importance is in the case of cellulose acetate. It is a solvent for cellulose nitrate, and greatly reduces the inflammability of cellulose nitrate compositions. This outstanding fire-resisting characteristic is one of the valuable properties of tricresyl phosphate. It is one of the leading plasticisers for polyvinyl chloride, in the synthetic rubber fields, etc. It has some disadvantages; for example, with nitrocellulose it tends to accentuate discoloration due to sunlight. The other important disadvantage is the fact that it is reputed to be somewhat toxic, and precautions have to be taken in this connection both in the handling of the material and the application of plastic products containing it.

Dimethyl Phthalate. Dimethyl phthalate is a clear water-white liquid having a specific gravity of 1·195 at 20°C., boiling at about 285°C. The solubility in water is 0·3 per cent. It is soluble in organic solvents and is compatible with most resins and oils. It is likewise a solvent for cellulose acetate and cellulose nitrate. As a consequence it is widely used in the preparation of plastics based on cellulose acetate in particular. This is in spite of the fact that it is fairly volatile material. It has good fastness to light and is non-toxic. Its leading application is in the preparation of cellulose acetate dopes and lacquers, the preparation of films and sheets for use in laminated safety glass.

Dibutyl Phthalate. Dibutyl phthalate is probably the most widely used plasticiser. It is a clear, water-white, odourless liquid. Its specific gravity is 1·047 at 20°C. The boiling point is 340°C., while the freezing point is −35°C. It is miscible with all common organic solvents and oils. It has low water solubility, ·001 per cent at 25°C. Apart from cellulose acetate it is used in almost all forms of plastic compositions; thus it is employed in making cellulose nitrate lacquers and plastics. It is widely used with ethyl cellulose. It is a leading plasticiser for use with polyvinyl chloride. It is also used with chlorinated rubber, synthetic rubbers, and so on. It has excellent light stability and is non-toxic.

Methyl Phthalyl Ethyl Glycollate. This is a typical plasticiser in this chemical class. It is a colourless non-toxic liquid, specific gravity 1·22, and a high boiling point. It has excellent stability towards light. It is miscible with organic solvents, except petroleum hydrocarbons.

It is not miscible with vegetable oils. It is one of the outstanding plasticisers for cellulose acetate and is also effective for cellulose nitrate. It finds application in plastic compositions based on alkyd resins, polyvinyl chloride, polystyrene, etc.

Triphenyl Phosphate. Triphenyl phosphate is a solid plasticiser, available as white flakes having a faintly aromatic odour. The melting point is 45°C., while the boiling point is about 390°C. It has a very low volatility, comparable with tricresyl phosphate. It has excellent resistance to moisture, its solubility being ·001 per cent at 25° C. It is soluble in most organic solvents and is compatible with oils and resins. It has high chemical stability. It is the outstanding plasticiser for the production of film and sheet from cellulose acetate. It has excellent compatibility with cellulose acetate, the retentivity being about 80 per cent. It imparts good flexibility and gives clear, tough composition.

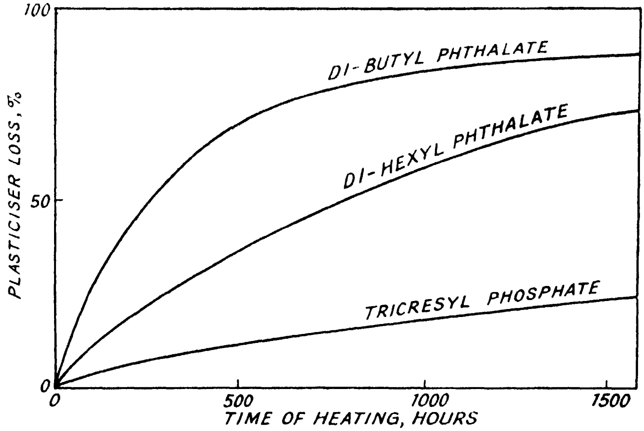


Fig. 197. Loss of plasticiser on prolonged heating of polyvinyl chloride compositions at 95°C.

Camphor. Until recent years camphor was obtained exclusively from the camphor tree which grows in Japan, Formosa, and China. It was virtually a Japanese monopoly. Camphor wood is digested with water, when camphor and camphor oil sublime with the steam. Camphor is purified by re-subliming. It is a colourless transparent material with pungent odour. The density is 0·922. It melts at 175°C., and boils at 209°C. It is used on an extensive scale, not only for celluloid plastics, but also for explosives and for therapeutic purposes.

Adequate supplies of camphor are now made synthetically in the U.S.A., in Germany, and in Great Britain. It is synthesised from pinene, which is obtained easily from turpentine.

TABLE 130

PROPERTIES OF SOME LEADING PLASTICISERS (LARGELY BASED ON THE FIGURES OF FORDYCE AND MEYER)[4]

	Mol. weight	M.P., °C.	B.P., °C.	Sp. gr.	Refractive Index	% water sol.
Butyl phthalyl butyl glycollate . . .	336	< −45	219 (5 mm.)	1·097	1·488	0·018
Butyl acetyl ricinoleate .	397	−65	—	0·940	1·461	—
Camphor . . .	152	178	204	0·990	—	0·170
Chlorinated diphenyl (Arochlor 1242)	—	−20	356	1·394	1·627	—
Chlorinated diphenyl (Arochlor 1248)	—	−9	350	1·456	1·630	—
Chlorinated paraffin (Cereclor 2)	—	—	260	1·230	—	—
o-Cresyl-p-toluene sulphonate . . .	262	52·5	—	1·207	1·558	0·003
Cyclohexyl-p-toluene sulphonamide	253	< 86	—	—	1·542	0·006
Diamyl naphthalene .	268	< −50	—	0·966	1·554	Insoluble
Diamyl phthalate . .	306	−55	—	1·022	1·488	0·010
Dibutyl phthalate . .	278	−35	325	1·050	1·490	0·013
Dibutyl sebacate . .	314	−12	345	0·933	1·493	0·005
Dibutyl succinate . .	230	−19	255	0·974	1·428	0·023
Dibutyl tartrate . .	262	22	312	1·098	1·445	0·485
Diethoxyethyl adipate .	290	−70	—	1·036	1·439	0·248
Diethoxyethyl phthalate .	310	< 34	345	1·123	1·492	0·195
Diethyl adipate . .	202	−14	245	1·002	1·426	0·060
Diethylene glycol dipropionate . . .	218	−82	165 (mm.)	1·056	1·429	3·60
Diethyl phthalate . .	222	−0.3	295	1·118	1·449	0·150
Diethyl sebacate . .	258	1·3	308	0·965	1·435	0·018
Diethyl succinate . .	174	−22	218	1·048	1·419	0·190
Diethyl tartrate . .	206	17	280	1·199	1·445	50
Dioctyl phthalate . .	390	—	240 (4 mm.)	0·984	—	Insoluble
Dimethoxyethyl adipate .	262	−16	210 (4 mm.)	1·075	1·439	1·420
Dimethoxyethyl phthalate	282	< −60	209–61 (20 mm.)	1·17	1·500	0·838
Dimethyl phthalate .	194	—	285	1·193	1·513	0·305
Dipropyl phthalate .	250	−31	158 (4 mm.)	1·071	1·494	0·015
Ethyl benzoyl benzoate .	254	58	355	1·155	1·573	0·010
Ethylene glycol diacetate .	146	−78	186	1·128	1·414	1·815
Ethylene glycol dibutyrate	202	−80	240	1·024	1·424	0·050
Ethylene glycol diproprionate . . .	174	−80	211	1·054	1·419	0·160
Ethyl phthalyl ethyl glycollate . . .	280	< −35	190 (5 mm.)	1·177	1·498	0·050
Mannitol hexaacetate .	434	< —	—	—	—	—
Methyl benzoyl benzoate .	240	< 52	351	1·190	1·587	0·005
Methyl phthalyl glycolate	266	< −35	189 (5 mm.)	1·220	1·503	0·053
o- & p-Toluene ethyl sulphonamide . .	199	18	—	1·190	1·540	0·140
Sorbitol hexaacetate .	434'	—	—	—	—	—
Sucrose hexaacetate .	582	84	—	1·347	—	—
Triacetin . . .	218	< −40	259	1·161	1·429	0·685
Tributyl citrate . .	360	< −55	—	1·040	1·444	0·008
Tributyl phosphate .	266	< −20	289	·0976	1·421	0·033
Tributyrin . . .	302	< −70	287	1·032	1·434	0·010
Tricresyl phosphate .	368	< −35	295 (13 mm.)	1·175	1·556	0·008
Triethylene glycol diacetate	234	< −60	300	1·111	1·437	50
Triethylene glycol dibutyrate . . .	290	< −70	154–60 (2 mm.)	1·033	1·437	0·800
Triethylene glycol 2-ethyl butyrate . . .	346	—	300	1·107	—	—
Triphenyl phosphate .	326	48·5	245 (11 mm.)	1·185	·563	0·002
Tripropionin . .	260	< −50	177–82 (20 mm.)	1·078	·431	0·313

Table 130 gives some of the chief physical properties of a wide range of plasticisers. Fig. 198 shows in graphical form the effect of heat on 14 plasticisers.

Choice of Plasticisers. The actual selection of suitable plastics is in general a matter of trial and error, and no hard-and-fast rule can be laid down. Clearly it is of importance that a plasticiser should be retained in a plastic condition, such as already indicated. If there is any appreciable loss, then articles will tend to shrink and buckle.

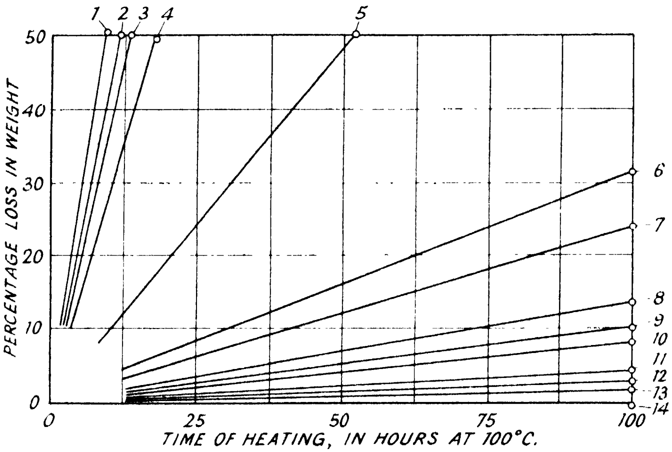


FIG. 198.—Free evaporation of some important plasticisers at 100° C.

1.—Triacetin. 2.—Tributyl phosphate. 3.—Dimethyl phthalate. 4.—Diethyl phthalate. 5.—Triethyl citrate. 6.—Dibutyl phthalate. 7.—Dibutyl sebacate. 8.—Butyl acetyl ricinoleate. 9.—Butyl phthallyl butyl glycollate. 10.—Dihexyl phthalate. 11.—Tributyl citrate. 12.—Dioctyl phthalate. 13.—Triphenyl phosphate. 14.—Tricresyl phosphate

Furthermore, the finish and appearance of products will be adversely affected. It should be clear that the general requirements of a plasticiser can be summarised as:—(*a*) it must be compatible with the basic material in fair quantity; (*b*) the plastic must not age by loss of plasticiser; (*c*) there must not be any chemical actions occurring which may affect the colour and properties of the plastic.

Types of Plasticiser. Several types of plasticiser are available operating according to their solvent action on the plastic base. They may be summarised as:

(1) *Solvent Plasticisers.* Members of this group first wet the synthetic material, are then taken up by it, swelling to a gel, and then form a colloidal solution or sol. Large quantities of such materials can be mixed, although the products will become extremely soft as the quantity

increases. There is a very close attraction between the two materials and it is difficult to separate them by physical methods. A typical example is dimethyl phthalate and cellulose acetate.

(2) The second type, which includes most standard plasticisers, also forms gels, even in low dilutions. The affinity between the materials is, however, not sufficiently great for the easy formation of solutions. In this type the tendency to separate is very small, although it can be affected by volatilisation.

(3) *Plasticiser Extender.* In this instance the material has a limited attraction for the basic material and will not cause it to gel, and often it will not mix at all. This type cannot be used as the sole plasticiser in the production of plastic materials, owing to the lack of affinity. It is very loosely bound and tends to sweat out quite easily.

On the other hand, if compatible plasticisers are present, then frequently large proportions of extenders may be added with advantage. The latter appear to be held in the compound by the true plasticiser. A typical example is the use of chlorinated paraffin, together with dibutyl phthalate in polyvinyl chloride compositions.

Mixtures of plasticisers are often used in order to obtain the best balance of properties.

At this point a sharp distinction must be drawn between plasticisers and lubricants; the latter are often added to plastics in small quantities, to facilitate processing. They should not be confused with plasticisers, since their function is quite different, and, indeed, there is no affinity with the plastic base.

The long molecules of the lubricants help the linear plastic molecules to slip over one another and also readily migrate to the surface and act as a lubricant between plastic and metal parts in processing, e.g. in extrusion, in moulding, etc. They are generally soaps or waxes, and include ethyl palmitate, calcium stearate, stearic acid, paraffin wax, etc.

Examples of Applications of Plasticisers. The most striking example of plasticiser is the behaviour of camphor in relation to cellulose nitrate. This was one of the earliest examples of the use of a plasticiser, and it still remains outstanding in this field of activity. Other examples include the use of tricresyl phosphate in polyvinyl chloride, the use of blends of plasticisers in cellulose acetate, and ethyl cellulose and so on.

Most materials having the primary characteristics, namely, high boiling point, have been tried as plasticisers in every type of plastic, yet comparatively few are employed in commercial practice. It is very interesting to note that the same range of plasticisers applies almost equally well for most types of plastics irrespective of chemical compositions. It would almost seem that some physical attribute is the really important factor. On the other hand, some materials are exceptionally good plasticisers for specific types of materials, e.g. tricresyl phosphate for polyvinyl chloride or for cellulose nitrate, but are of comparatively little use for others, e.g. for cellulose acetate. There are exceptions where a material has a specific influence, notably the case of camphor in nitrocellulose.

Some of the standard plasticiser combinations for industrial use are as follows:

Cellulose acetate; dimethyl and diethyl phthalates; triphenyl phosphate for reducing inflammability and raising the softening point; sulphonamides except where light stability is required; methyl phthalyl ethyl glycollate and methoxy-ethyl phthalate.

Cellulose acetobutyrate; phthalates and tripropionin.

Cellulose nitrate (11 per cent nitrogen for plastics); camphor, tricresyl phosphate.

Cellulose nitrate (12 per cent for artificial leather); castor oil.

Polyvinyl chloride; dibutyl phthalate for elasticity, dibutyl sebacate for low temperature, flexibility; higher phthalates such as hexyl, octyl, capryl, or butoxyethyl; tricresyl phosphate for low loss on heating.

Polyvinyl chloride-acetate; dibutyl phthalate, dihexyl phthalate, dioctyl phthalate and tricresyl phosphate for special purposes.

Polyvinyl butyral; dibutyl sebacate, triethylene glycol dihexoate and similar polyglycol esters.

Ethyl cellulose; phthalates, chlorinated diphenyl; mineral oils, castor and other vegetable oils for rubbery characteristics.

Plasticisers only emphasise the inherent characteristics of the basic material. If they are there, then the plasticiser will bring them out. If they are not there, then the plasticiser will have no influence. For example, unless there exists in the basic material conditions for certain properties, e.g. toughness, etc., the typical characteristics of high polymers, the plasticiser cannot confer them. In the case of materials having different chain lengths (different molecular weights), for example, cellulose acetate or ethyl cellulose, no amount of plasticiser will give the same strength characteristics in the short chain material as can be obtained in the long chain material.

Existing Theories. A number of theories have been put forward to explain the action of a plasticiser.

In many cases the plasticiser ability is indicated by a tendency for the plastic base to gel in the plasticiser, after the manner of gelatine and water, either on standing or when warm. De Bell[1] visualises the plasticiser molecules attaching themselves to the plastic base by virtue of the attraction between some of their chemical groups and specific groups on the large base molecule, so that they hold the long molecules apart and permit them to slide over each other with considerable freedom.

According to Ott,[9] a plasticiser swells a long chain, e.g. the cellulose chain. In this way the chains are pushed farther apart, and the bond of attraction between neighbouring chains is reduced. The behaviour of camphor in celluloid illustrates this. Nitro-cellulose chains appear to possess strong attractive forces, due probably to the small compact nitrate groups. To plasticise nitro-cellulose it is, therefore, necessary to choose a material having a powerful solvent action; that is to say, something which can push the chains apart and attach itself to the nitrate groupings. High compatibility is thus necessary, and the material will be uniformly distributed. Camphor does this and appears to form a stable grouping associated with the nitrate groups. The large camphor molecules are able to hold the cellulose chains well apart except at rare intervals, where the chains may be strongly held. In this the tendency will exist for long stretches of chains to be faintly attracted to adjoining ones, while free to move under heat influence. The occasional linkage with a neighbouring molecule prevents cold flow. In many senses this system resembles vulcanised rubber; and, indeed, celluloid actually does show considerable elasticity.

Elam, Preusser and Page[3] have examined the work carried out on plasticisers and conclude as follows:

A plasticiser is added to a resin in order to impart toughness and flexibility. An attempt to explain the mechanism whereby these changes in physical properties are produced is necessarily somewhat speculative. The polymer may be considered as a mass of chain molecules, each possessing a linear dimension that is very large compared with the cross section. The vinyl-type resins are composed of units, each of which contains polar groups, and these groups give rise to forces of attraction which hold the mass together in a rigid compact structure.

Polymers which do not have large side groups (polyvinyl chloride, for example) may have regions of regular spacing which are described by Mark[7] as crystalline.

One function of a plasticiser is to offer to the polymer molecule polar groups which will be attracted by the polymer in preference to polar groups from another polymer chain. This causes dissolution of the polymer by relaxation of the forces between adjacent chains, and permits the chain segments to slip past one another under mechanical stress.

Expressed in another way, the plasticiser molecule is interposed between two polymer chains and is less strongly attracted than the chains are to each other.

Another function has been termed a "lubrication" action, which supposedly facilitates the gliding of polymer chains past one another. It is possible that this effect is related to a "bulking" process, wherein the plasticiser, which associates with the resin, effectively creates new side groups and prevents the chains from fitting into a more or less regular lattice structure.

A general pattern for designing plasticisers has been suggested by Kirkpatrick.[6] The presence of highly polar groups (O attached to S, P or C) favours compatibility with a highly polar resin. If the plasticiser has a long chain structure, the polar groups are preferably to be distributed along the chain. Similarity in shape between the plasticiser and monomer is desirable; at least it seems advantageous that the polar groups of the plasticiser should be in a geometrical pattern of polarity which complements that of a resin segment.

According to Ivanova and Rogovin,[5] a plasticiser that is capable of dissolving the cellulose ester, e.g. a solvent plasticiser, causes a regular decrease of strength (ultimate tensile) with increasing quantity of plasticiser. A non-solvent plasticiser will, in small amounts, make the product stronger. On further increase of plasticiser the strength falls, as with the solvent type.

It may be said that the solvent plasticiser is capable of overcoming, by itself, the high cohesion in the crystalline structure, and a non-solvent plasticiser adheres to the ester in amorphous regions, or after the regular lattice has been disrupted by a volatile solvent.

TABLE 131

INFLUENCE OF CHEMICAL PLASTICISING

	% Vinyl chloride	Softening Point	Softening Point 100 polymer/50 T.C.P.
Polyvinyl chloride . .	100	about 180° C.	85° C.
Polyvinyl chloride-acetate .	95	about 150° C.	75° C.
Polyvinyl chloride-acetate .	88	about 130° C.	65° C.
Polyvinyl acetate . . .	—	38° C.	—

The Action of Plasticisers. Strength and toughness are characteristics of long-chain molecules, e.g. of typical plastic materials. The molecules must also be in close proximity so that if there are very long or bulky side groups which keep the main chains far apart they will tend to be soft and lacking in strength. In fact, the introduction of bulky side groupings is one method adopted in synthetic chemistry to soften refractive high polymers. Consequently, an effect somewhat similar to that produced by plasticisers is attained by chemically combining suitable groups directly on the molecule itself. Thus, in polyvinyl chloride-acetate, the acetate group serves to act as a plasticiser even though additional plasticisers may be required. The amount of additional plasticiser required to get equivalent plasticity will be much less than with straight polyvinyl chloride. The more acetate groupings present, the softer and more amenable to processing the material becomes.

This technique of effecting plasticisation by chemical methods has been closely studied. Its influence is apparent in many commercial plastics.

Spacing Effects in Chemical Plasticisation. It is interesting and instructive to consider how introduction of side chains profoundly affect the plastic behaviour. Consider polyvinyl chloride and polyvinyl chloride-acetate copolymer. It should be made quite clear that consideration is only given to ideal sections of chains and that the effects are three-dimensional.

TABLE 132

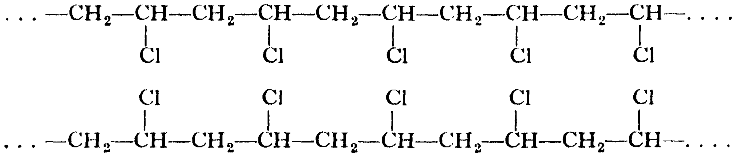
INFLUENCE OF CHEMICAL PLASTICISING ON AMOUNT OF ADDED PLASTICISER REQUIRED TO GIVE SAME FLOW TEMPERATURE[4]

	Parts dimethyl phthalate to give flow at		Parts diethyl phthalate to give flow at		Parts dimethoxyl phthalate to give flow at	
	266° F.	307° F.	266° F.	307° F.	266° F.	307° F.
Cellulose acetate (38·5% acetyl)	37·8	22·6	59·5	38·7	62·5	39·6
Cellulose acetobutyrate (37% butyryl and 13% acetyl) .	15·8	6·3	17·0	7·0	18·5	7·8

These adjoining sections of two polyvinyl chloride chains (Fig. 199) are in close proximity. Between them there exist considerable cohesive forces (or Van der Waal's forces) largely due to attraction between the chlorine atoms. These forces are strong enough to resist separation or thus prevent easy flow when the temperature is raised. Where vinyl acetate groups are introduced and a copolymer is formed the picture is rather different (Fig. 200). Consider two adjacent chains of a copolymer.

Introduction of the acetate group quite clearly spaces the long chains apart and, consequently, greatly reduces the cohesive forces. As a result the softening point is lowered and less added plasticiser is required to attain any desired plasticity.

The spacing effect is exaggerated on the diagram since the likelihood of acetate groups coming opposite each other will be comparatively small until the concentration of acetate reaches a high value.



$$\ldots-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-\ldots$$

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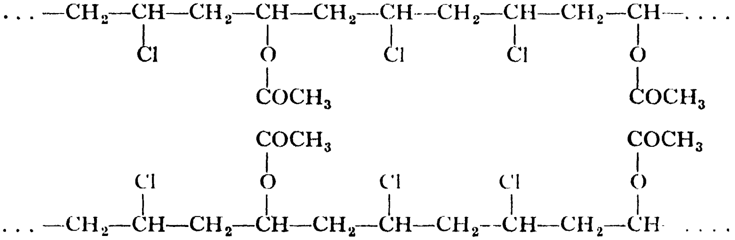
Fig. 199. Theoretical juxtaposition of two polyvinyl chloride chains

This general principle seems to work out in practice. Consider acrylic ester plastics. (Fig. 201.)



$$\ldots-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{\underset{\underset{COCH_3}{|}}{O}}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{\underset{\underset{COCH_3}{|}}{O}}{|}}{CH}-\ldots$$

$$\ldots-CH_2-\overset{\overset{Cl}{|}}{CH}-CH_2-\overset{\overset{\overset{\overset{COCH_3}{|}}{O}}{|}}{CH}-CH_2-\overset{\overset{Cl}{|}}{CH}-CH_2-\overset{\overset{Cl}{|}}{CH}-CH_2-\overset{\overset{\overset{\overset{COCH_3}{|}}{O}}{|}}{CH}\ \ldots$$

Fig. 200. Adjoining polyvinyl chloride-acetate chains

These are adjoining portions of two ethyl acrylate polymer chains. If the ethyl group is replaced by propyl or butyl or longer groups the materials become softer and softer, i.e. the chains are being spaced farther and farther apart.

Consider ethyl acrylate polymer in comparison with methyl methacrylate polymer, with which it is isomeric. (Fig. 201.) The latter is much harder and the reason seems fairly easy to explain. The side chain—the spacer chain—is distinctly shorter.

The methyl group attached to the main chain will have little influence on the spacing.

As the side chain (or spacer chain) in methacrylate becomes longer, i.e. ethyl is replaced by propyl, butyl, etc., the polymers become softer and softer. In fact, with an exceptionally long group such as lauryl the material is liquid.

The most admirable illustration of this principle is perhaps seen with butyl methacrylate polymers. There are three butyl alcohols: normal, secondary and isobutyl, each of which polymerises and which give corresponding groupings in the polymers. So the unit in each chain is respectively as shown in Fig. 202.

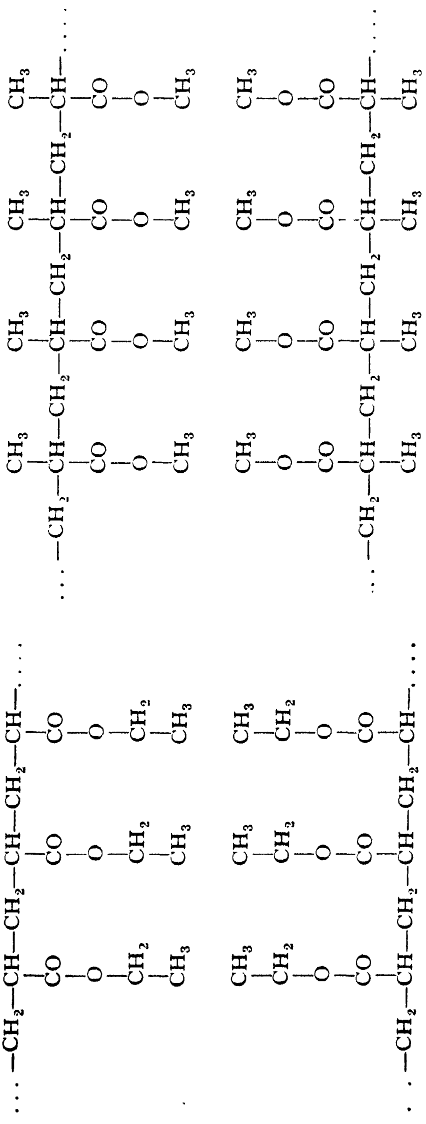


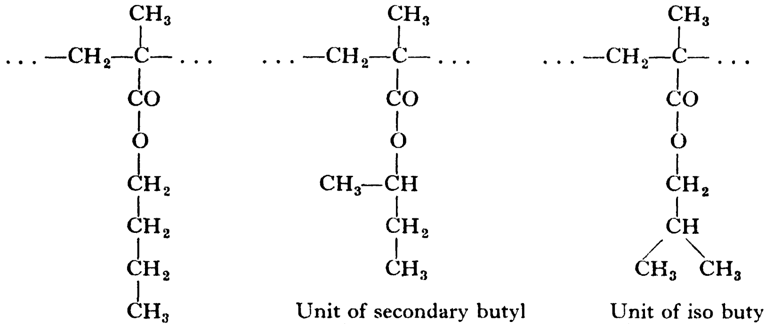
Fig. 201. Comparison between ethylacrylate chains (left) and methyl methacrylate chains (right)

According to the spacer theory n-butyl methacrylate polymer should be softer than secondary, which in turn should be softer than the iso-compound. The softening points are:

n-butyl methacrylate polymer . . .	33°C.
Secondary butyl methacrylate polymer .	62°C.
Iso-butyl methacrylate polymer . .	70°C.

In the case of polystyrene the linear chain is considered to have the flat benzene hexagon sticking out at regular intervals. Two adjoining chains will tend to interlock like a zip fastener. (Fig. 203.)

Flow will be extremely difficult until temperature conditions are sufficient to push them apart.



Unit of n-butyl methacrylate polymer

Unit of secondary butyl methacrylate polymer

Unit of iso butyl methacrylate polymer

Fig. 202. Units of the higher methacrylate polymers

If a plasticiser is added, e.g. tricresyl phosphate, the chains are pushed apart and the softening point drops to such an extent that the material becomes too soft for most commercial applications.

In the alkyd resins the monobasic fatty acids perform a similar function. In cellulose acetobutyrate, the butyric acid helps to soften the plastic. Its presence makes necessary only small amounts of additional admixed plasticisers. Similar molecule effects are seen in the oil-soluble curing types of resins, as, for example, the butyl ether groups in the urea resins used for industrial finishes.

Some phenomena are difficult to explain. Thus tricresyl phosphate is an excellent all-round plasticiser. Yet it is quite incompatible with cellulose acetate, and is not used. On the other hand the closely related triphenyl phosphate is one of the leading plasticisers for cellulose acetate.

Relationship between Chemical Plasticising Action and Addition of Plasticisers. It has been indicated that the essential feature affecting plasticity of long chain polymers is to get the long chains apart, so that they can pass each other and flow. In copolymers and in polymer design the pacing is achieved by the introduction of the long spacer groups by chemical methods.

This spacing effect illustrated by chemically combined copolymers, and polymers with long side chains, provides a useful parallel for plasticiser action. The effect of added plasticisers may be more marked only because relatively large quantities are used.

Plasticisers act as detached spacers. They will, to some extent, be attracted to the long chains. If this attraction is high they may in effect be attached to the long chains albeit by forces which are much weaker than exist with the spacer groups. The affinity will be shown by the tendency for gelling, which indicates the building up of a three-dimensional structure. The long molecules will thereafter tend to become so effectively and evenly spaced out that solution becomes possible.

Where the attraction between plasticiser molecule and long chain is less than in the previous case, then the spacer effect is achieved with little or no degree of attachment. If attraction is present up to a certain degree a gel may be formed, but solution will not be possible. There will be sufficient holding force to prevent the plasticiser moving.

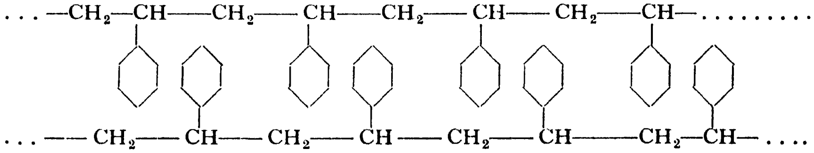


Fig. 203. Two adjoining polystyrene chains

The extreme case is where the material will act as a spacer, but with no effective attachment to the long molecule. It is free to move and does so, migrating and tending to sweat and bleed out to the surface.

Different plasticisers will vary between these conditions, according to the specific attraction existing between it and the long chain polymers. It is possible for a good plasticiser to mix in with a bad plasticiser, and yet have an increased effect, i.e. the poor material acts as an extender. In this case the poor plasticiser can clearly exert its spacer effect and be held in by its attraction, not to the long chain, but to the plasticiser molecule.

These principles work out in practice. The four types of plasticisers may thus be summarised as:

(*a*) Copolymerisation, which affords a chemical spacer between chains.

(*b*) Solvent plasticiser which acts as a chemical-physical spacer.
(*c*) Ordinary plasticisers which act as physical-chemical spacers, and
(*d*) Extenders which act as physical spacers.

Cheney[11] has recently reviewed the subject of plasticisers.

REFERENCES

1 De Bell. *Modern Plastics*, 1942 (November), 89.
2 Durrans. *Solvents*, Chapman & Hall, Ltd., 1944, 5th Edn.
3 Elam, Preusser and Page. *Ind. Eng. Chem.*, 1943 (May), 95.
4 Fordyce and Meyer. *Ind. Eng. Chem.*, 1940, **32**, 1053.
5 Ivanova and Rogovin. *J. Applied Chem.*, U.S.S.R., 1938, **11**, 1948.
6 Kirkpatrick. *J. Applied Physics*, 1940, **11**, 255.
7 Mark. *Nature*, 1938, **142**, 937.
8 Mellan. *Industrial Solvents*, Reinhold Publishing Corp., 1939.
9 Ott. *Ind. Eng. Chem.*, 1940, **32**, 1643.
10 Cheney. *India Rubber World*, 1948, **119**, 212.

CHAPTER XXIII

THE EXTRUSION PROCESS

THE extrusion process is one of the most important methods for handling plastics. It has been a familiar process for many years. It has the outstanding production advantage of being a continuous process. Owing to its continuity it is responsible for the manipulation of a very large proportion of thermoplastic materials.

Tubes and rods are made to very accurate dimensions. Strips of various cross sections are extruded in unlimited lengths. In all cases the emphasis is on maintenance of strict dimensions. This is also true for the covering of wires, cables, strings, fibres, etc.

Most of the leading thermoplastics are extruded. Notable examples include polyvinyl chloride and copolymer, cellulose acetate, ethyl cellulose, etc. These have no solvents present and extrusion is carried out at higher temperatures. Low temperature extrusion is employed for materials such as cellulose nitrate compositions, cellulose acetate, casein, etc., which for these purposes are made up into doughs containing solvent.

The process has been used for the handling of rubber for about a century, and is not in any way new or recent. The principle involved is straightforward. Thermoplastic material is heated to make it plastic, is pushed through a die, and is then cooled. Under extrusion it takes up the shape of the die.

The process is carried out generally on screw type machines. The principle is, in fact, that of the standard sausage machine with which everyone is familiar. The screw should be driven by a variable speed motor. Another less widely used form of extrusion is that employing a piston fitting into a heated chamber containing the plastic material. Under the pressure the plastic material is forced through an aperture containing the die.

Any plastic screw extrusion machine functions by the differential of the frictional forces exerted by the material on the screw and against the cylinder wall. For this reason every effort is exerted to decrease the frictional force on the cylinder wall, while maintaining a suitable degree of plasticity.

Screw extrusion machines are composed of a screw rotating in a horizontal tube. The screw is of a modified Archimedean type. An aperture in the tube at the beginning of the screw allows for feeding the plastic material into the machine. At the delivery end of the screw attached to the horizontal tube is a metal head strong enough to withstand the high pressures developed. The die is fitted into this head. The screw on a 2-inch machine may develop as much as 50 tons per sq. inch. Where the plastic is being extruded over some other material, e.g. over wire as for cables, or over string or threads for ropes, etc., the extrusion head is normally fitted at right angles. Thus the cable industry uses large numbers of such extruders. In this instance there is a device whereby the flow of plastic material is uniformly distributed at right angles to the initial direction.

Fig. 204. Extruding cellulose acetate tubing[6]

In recent years there have been modifications so that wire, etc., has been passed through the machines at an angle. Most recent trends seem to be to have wire, etc. passing through the screw itself so that extrusion is a straight-through procedure and obstruction to flow imposed by any change of angle, is eliminated.

Generally, every part of the arrangement may be heated, either being provided with jackets through which a heating medium can pass, or alternatively with electrical heating devices. In most instances a temperature gradient is maintained. In normal practice the temperature is lowest at the feed and highest at the die.

The heat supplied in this manner has the effect of softening the plastic, while the screw kneads the material to a soft plastic condition, and eventually forces it through the die at a constant rate. Material at the feed section when carried along the screw is heated by coming in contact with the barrel and made partially plastic by working the compound under the back pressure created. The material is forced into the head and through the extrusion die. The chief problems are to maintain a constant rate of feed uniformly, and maintain a constant rate of extrusion.

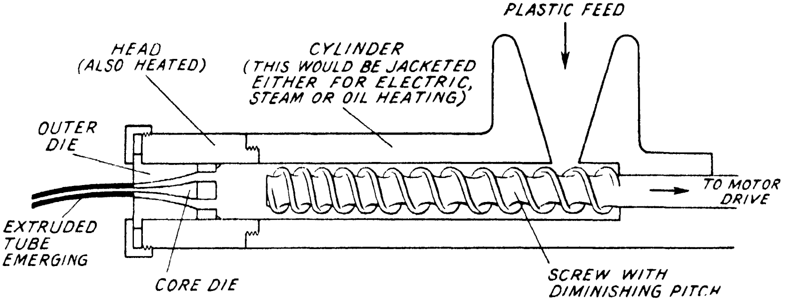


Fig. 205. Sketch of extruding machine

Naturally, the technique adopted will vary with each type of thermoplastic. Plastic materials are generally available as granules, shreds or strip. Granules or shreds imply the necessity for feeding hoppers. Strip may be handled along the lines used for rubber, i.e. being fed direct on to the screw or more generally on to a feeding roller. Prewarming is widely practised especially in the case of strip or lump materials, to facilitate the material being grasped by the screw and the maintenance of a constant feed. With some materials such as polyvinyl chloride, the material is often premilled before feeding into the machine.

Certain elementary design requirements are evident. The machine should be streamlined, thereby eliminating any obstructions to the flow, and avoiding any nooks and corners where material may become lodged. If plastics do fill up such parts they may become overheated and will eventually decompose, subsequently coming out as knobbly discoloured lumps, and giving unsatisfactory extrusions. They will also lodge in the die thus breaking up the flow of plastic. For the same reason it is desirable not to have any internal threaded parts where plastics may lodge. The existence of such points may cause difficulties in cleaning and dismantling machines.

The machine should be designed to achieve rapid and thorough heat plasticising under controlled conditions but avoiding overheating. The softened plastic should pass through the machine as rapidly as possible. A number of methods have been adopted for heating; steam provides adequate temperatures for rubber and a number of plastics such as polythene and is widely used. The advantage of steam is that accurate control can be achieved. Heated oil is another extensively employed heating medium. Electrical heating is likewise fairly extensively used. In most instances thermostatic controls are employed wherever possible.

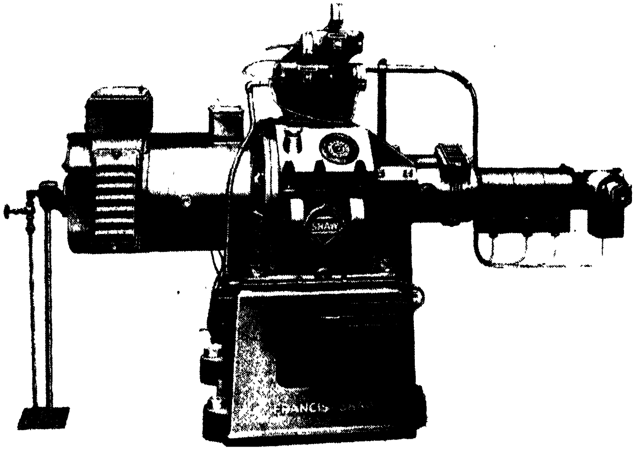


Fig. 206. Typical extruder with right-angled head for covering wire[8]

The material of which the extruder is made requires important consideration. The materials of construction of the screw and barrel are important. They must withstand severe mechanical forces and should exert no specific catalytic effect on the decomposition of the compound being extruded. For this reason cylinders are made of hardened corrosion-resistant ferrous alloys. The screw should be of stainless steel, or a tough, rigid steel. With many plastic materials operating at high temperature corrosive conditions develop, so that an extruder which may be well suited for an inert plastic material may rapidly corrode with other materials. Such influences are particularly noticeable with materials such as polyvinylidene chloride.

There are a number of factors to be considered in conjunction with the extrusion machine itself. These include the design of the die, the question of carrying away the extruded material, and also the collection of the material.

Some Design Requirements of Modern Extruders. The main differences between the rubber extruder and the plastic machine are: the cylinder and screw are approximately one-third longer; provision has been made for the insertion of a breaker plate and screens; and the thrust sections are more ruggedly built so as to absorb the increased back pressure developed. Variable pitch screws are preferred to constant pitch screws because they develop greater pressure.

The clearance between the screw and wall of the cylinder is extremely important, because of the relation between this clearance and pressure developed. This clearance should preferably be ·005 inch on each side of the screw, and in no instance in excess of ·015 inch on each side. Greater clearance between the screw and cylinder wall allows the material to wash back over the screw, resulting in loss of extrusion pressure. This leads to slow, uneven extrusion.

The speed of the screw varies for different materials, die shapes, and sizes. For this reason variable speed drives are most desirable. For example, a desirable screw speed for processing vinyl resin plastics is between 12 to 50 r.p.m.

The accurate maintenance of temperature conditions throughout is of fundamental importance.

Present practice tends towards the use of breaker plates and screens in the extruder in order to effect uniform plasticising of material passing through.

The size and design of the breaker plate used depends on the type of extruder. According to Intemann,[4] a 4-in. diameter strainer plate with a 3¼-in. working diameter, and having thirty-six ⅜-in. or ninety-six ⅛-in. diameter uniform bore holes, will produce good results when used in a machine with a screw of about 3¼ in. diameter. The strainer plate may be chromium-plated. Screens of various mesh and wire sizes can be used in combination with the breaker plate. One 20-mesh steel wire screen used with the breaker plate aids in obtaining satisfactory delivery speeds with good quality product. Fine screens may cut down the delivery rate of material.

The Nature of the Die. The design of dies for extrusion is not a simple matter. Design will largely be controlled by the nature of the plastic, especially such factors as plasticity at the extrusion temperatures. Obviously the design will depend on the shape and size of the product being made. Extrusion may be carried out along two systems. True extrusion is a precision process where material is extruded to exact dimensions. The other practice is to extrude above dimensions and draw the product down to the correct size.

The properties of the product may vary according to the method practised, even though the one plastic is being used. The factors of shrinkage and elastic behaviour must also be considered. In any event the evolution of the right type of die for any specific product is a matter of trial and error. Theoretical considerations rarely answer the problem conclusively.

The system of centralisation of dies is a matter of some difficulty. This applies in particular to tubing and to the covering of a core, e.g. wire, rope, etc. The traditional rubber method is to have four adjustable screws. In plastics practice the trend is towards having self-centring dies. It is a fortunate circumstance that dies are small articles which are readily made and lend themselves to experiment.

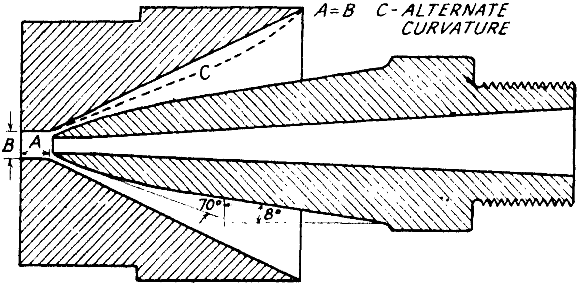


Fig. 207. Typical set-up of dies for extruding vinyl plastics. In making tubes the centre hole would be blocked[4]

The design of dies will depend largely on the nature of the material being extruded. Thus the shape for extruding an elastic rubbery material such as polyvinyl chloride will be different from that used to handle the deader, less springy polythene.

Because of the elastic nature of the vinyl resin compound, an expansion of about 25 per cent, depending on the die strength and shape, will occur as the stock leaves the die. This expansion is often compensated for—and size control benefited—by a controlled stretching of the product as the compound leaves the die. For this reason, and also to cope with naturally variable extrusion rates, it is preferable to use a variable speed drive on the capstan.

As a general guide, according to Intemann, the bearing length or parallel part of the forming die is the same length as the diameter of the die for sizes up to ½ in. in diameter. For sizes larger than one-half of an inch the bearing length is often kept constant at one-half of an inch for all sizes.

The die diameters are usually made 3 to 5 per cent over that of the average outside diameter being extruded. The necking down, or stretching of the compound at the die, improves the finish.

Taking off Extruded Material. The material will come out of the die orifice at a more or less rapid rate, according to the rate of extrusion, still hot and thermoplastic, and consequently easily deformable. It must, therefore, be taken away under such conditions that deformation is avoided, otherwise the whole object of the extrusion is defeated. Where tubings, etc., of large dimensions are being made, the end is sealed and air is blown into them in order to maintain the shape and help the cooling.

In general, extruded materials are carried away on a moving belt, normally a fabric belt. Streams of water or blasts of cold air are used to set materials. There are instances where refrigerated cooling systems are employed. Cooling of materials must likewise be carefully controlled in order to avoid unnecessary strains and alterations in shape. The shrinkage of the plastic being handled is decidedly of considerable significance, a typical example being polythene. The inherent properties of the particular plastic being handled will necessarily be a deciding factor in the form of haul-off adopted.

The final operation in extrusion is the collection of the material. In some instances, e.g. tubes for pens and pencils, furniture trims, the materials are not required in continuous lengths, and are cut to size as soon as cold. On the other hand, flexible tubings, rods, and covered wires must be produced in the form of coils. Consequently it is necessary to devise suitable collection equipment to take this. It is usual to have automatic haul-off gear which is synchronised with the extrusion process. It is usually geared up with the driving gear of the extruder.

Plastics for extrusion are generally compounded specially. Additions of materials such as lubricants and stabilisers are necessary. Some materials such as polyvinyl chloride or cellulose acetate, are available either as soft, tough, flexible materials, or they may be hard and rigid. These are formulated to make the extrusion temperature range as wide as possible, and to promote retention of shape while cooling.

In all cases of extrusion, the plastics must be dry in order to obtain best results. The presence of a very small amount of moisture in the hot extruding section is sufficient to cause blistering and roughness.

Most of the thermoplastics, with the exception of the cellulose nitrate group, can be extruded along the lines indicated. Each type requires a special technique, for every material has its own idiosyncrasies. The vinyl chloride polymers and copolymers can be extruded in properly designed machines and yield products which vary from the hard, brittle, and rigid type, to those which exhibit remarkable toughness and flexibility. Cellulose acetate plastics can also be extruded; in fact, they have been fabricated in this manner for many years. Ethyl cellulose is extensively used as extruded material.

The field for extruded plastics grows continually wider. Woven strips and rods tend to replace reed, rattan and straw. Filaments are being woven into new types of fabrics either having special characteristics for industrial purposes, or offering new effects for decorative use. The use of trims and mouldings in the building industry is another angle.

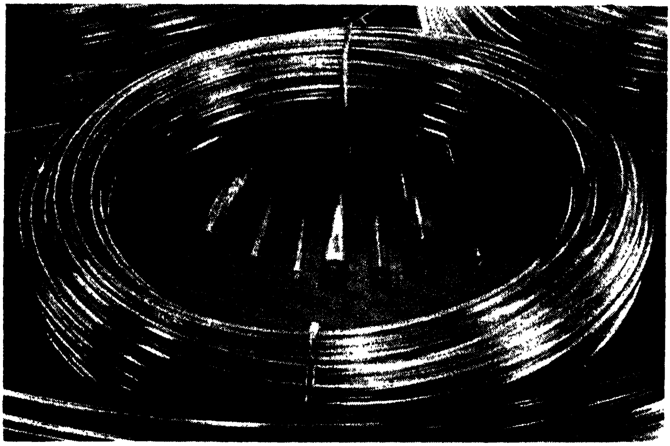


Fig. 208. Typical extruded tubes

Polyvinylidene chlorides involve special technique; so does nylon in the production of monofilament. This is because higher temperatures are involved and in addition the materials have to be drawn to develop their desired characteristics.

Extrusion of Polyvinyl Chloride Compositions. Up to the present time polyvinyl chloride has attained its great importance largely owing to its suitability for extrusion.[2] It is, of course, the most widely used plastic for covering wires and cables, and making tubes. Consideration of the conditions applying in these applications throws much light on extrusion technique generally. The conditions involved have been described by Barron, Dean, and Scott.[1]

All grades of polyvinyl chloride are best extruded in a machine specifically designed to handle thermoplastic materials. Up to the present time in Great Britain large quantities of polyvinyl chloride have been extruded on machines designed to handle rubber. Only quite

TABLE 133

PROPERTIES OF LEADING THERMOPLASTICS APPLIED BY EXTRUSION

Material	Outstanding Properties	Use Limitations	Leading Applications
Cellulose acetate and aceto-butyrate	Ease of fabrication Uniformity Dielectric strength	Extremes of temperature Solubility Moisture absorption	Pens, pencils, etc. Furniture trims Interior trims Ribbons, etc.
Ethyl cellulose	Ease of fabrication Uniformity Dielectric strength Resistance to impact at low temperature	High temperatures Solubility Moisture absorption	Insulations Ribbons
Acrylates	Clarity Dimensional stability Weather resistance Rigidity Dielectric strength Uniformity Ease of fabrication	Rigid	Electrical parts Rods and tubes Transparent optical purposes
Polyvinyl alcohol	Elasticity Solvent resistance	Water solubility	Synthetic pliable tubes
Polystyrene	Superior dielectric strength Low power factor Dimensional stability	Brittleness	Transparent and electrical sections Drawn fibres
Polyvinyl chloride and Polyvinyl chloride acetate	Elasticity as desired Chemical resistance Dielectric strength Water resistance Dimensional stability	Low softening point	Insulation Sheathing Fibres Tubing
Polyvinylidene chloride	Superior chemical resistance High softening point Dielectric strength Flexibility Lack of cold flow	Brittleness at low temperature	Tubing to replace metal Corrosion resisting
Polythene	Electrical characteristics Toughness Corrosion resistance	Softness	Electrical insulation
Nylon	Toughness Corrosion resistance	High temperature	Fibres Monofilament

lately have specially designed machines become available. As already indicated such extruders differ from the older types chiefly because they can be operated at much higher temperatures. A longer screw is now regarded as preferable for thermoplastics generally. In up-to-date machines screw and cylinder are generally about one-third longer than in the older types. The newer extruders are designed to allow the plastic to flow as freely as possible, being streamlined, in order to avoid dead corners where the material could become overheated.

Screws having either a single or double lead for material may be employed for extruding polyvinyl chloride. The only difference in results with these two types is that there is a rather higher extrusion pressure with the single lead. In actual service it is found that screws designed with a decrease in pitch from the feed to the die are best.

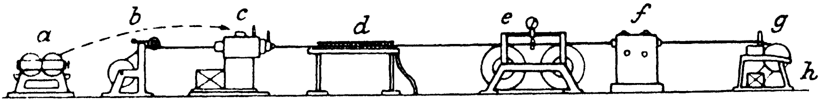


Fig. 209. Extruding polyvinyl chloride
(*a*) mixer, (*b*) wire coil, (*c*) extruder, (*d*) cooling, (*f*), (*g*), (*h*) testing and collecting

The older type extruders can be used to handle polyvinyl chloride if the head is heated to the required temperature. This object is attained by using electrical heating, circulating hot liquid, hot oil, or high pressure steam.

Polyvinyl chloride is generally preheated before being fed into the extrusion machine. If it is fed cold into an unsuitable machine then uneven lumpy products are often obtained. Smooth finish depends entirely on the uniformity of the material as it passes through the die. It is necessary to work the stock on a mixing mill in order to make it sufficiently plastic, so that when fed to the heated extruder the screw will convey the material forward to the head and die in a uniform condition. Without this pre-working there are invariably semi-plastic particles dispersed in the somewhat plastic mass which form lumps or cause pinholes, often resulting in failure of insulation. With the rubber type extruders using the material oven-heated there is adequate frictional working of the compound. Another disadvantage is that the delivery head working at right angles to the screw, so widely used for wire covering, is not streamlined. So that pockets of materials are formed in which polyvinyl chloride compound lodge and eventually decompose. The material can be handled cold on specially designed extruders with most satisfactory results.

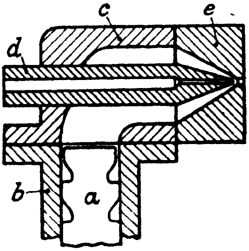


Fig. 210. Cross-section of rectangular-feed-type extrusion head
(*a*) feed worm, (*b*) heated cylinder, (*c*) die head, (*d*) lead-in for wire, (*e*) mouth of die

A high surface gloss can be obtained by working with a high temperature on the die. The temperature on the die may be 160°–170° C. or even higher, but since polyvinyl chloride begins to decompose around 180° C. care is necessary. The plastic must not be subjected to this temperature for any length of time.

Preheating. Preheating may be carried out in ovens, in another extrusion machine, or preferably on hot rolls or in an internal mixer.

A large oven fitted with at least two compartments is generally used so that whilst polyvinyl chloride is being used from one compartment, another batch is being heated. Polyvinyl chloride should be cut into short strips, say 8 inches long, and heated to between 100° C. and 120° C. on trays. Polyvinyl chloride chips are particularly suitable for heating in ovens. The size of the oven required will depend on the size of the extruded section being made.

Hot Rolls Method. Polyvinyl chloride may be prewarmed on rolls at a temperature of about 120° C. When a smooth sheet is formed on the rolls it can be fed immediately to an extrusion machine. Care should be taken not to overheat polyvinyl chloride on the rolls and not to roll it for long periods, which would result in slight loss of plasticiser.

Haul-off Gear. Owing to the high rate of extrusion of polyvinyl chloride, special equipment is required to handle the extruded section. Light sleevings can be made without the use of haul-off gear, the sleeving being allowed to coil on a cone on the floor underneath the die.

However, in covering cables and wires expensive and complex haul-off equipment is unavoidable.

Covered wire should be cooled after leaving the die by a long travel through air or by passing through cold water in a long trough. The following special equipment for handling plastic extrusion compositions are involved in covering wires and cables:

(1) Spools for holding reels of wire.
(2) Wire-straightening guides.
(3) Wire-tensioning drums, for drawing the wire through the die at a speed which can be altered by variable gears.
(4) Cooling troughs.
(5) Electrically driven wind-up bobbins with a traversing device for even winding.

Start of Extrusion Process. Before starting extrusion of the required section, the polyvinyl chloride in the head of the press should be at a steady temperature, and this can best be attained by extruding a few pounds of composition through the bleed-off tap, or, if no such device is fitted, through the die. Since polyvinyl chloride is thermoplastic it can be reworked, but care should be taken to prevent contamination.

Dimensions of Extruded Section. The maximum size of section which can be extruded depends largely on the size of the extrusion press and the thickness of the section. If polyvinyl chloride is extruded without tension there is a slight swelling of the section as it leaves the die, and the diameter of the extruded section is greater than the diameter of the die, but a section under tension will be drawn down and the diameter will be less than diameter of the die.

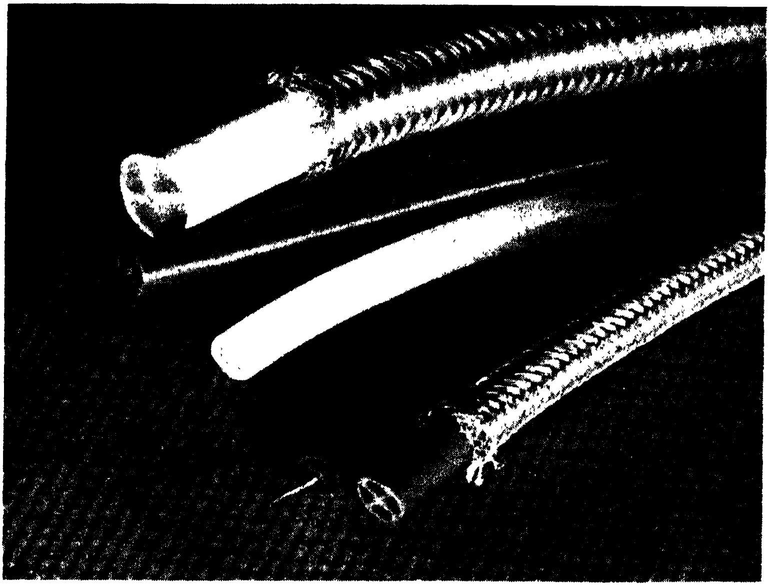


Fig. 211. Some typical products extruded from polyvinyl chloride[7]

The dimensions of the extruded section depend on:

(1) Dimensions of the die (with a long die there is less difference than with a short one between the dimensions of the die and those of the extruded section).
(2) Grade of polyvinyl chloride.
(3) Speed of screw.
(4) Speed of haul-off.
(5) Temperature of extrusion.

Veit[5] has touched on the possibilities of covering several wires simultaneously.

Similar considerations apply to the extrusion of other products, although the details will obviously depend on the type of plastic being employed, and the design of the product being extruded.

The most recent consideration of the subject of extrusion has been the paper by Fortner.

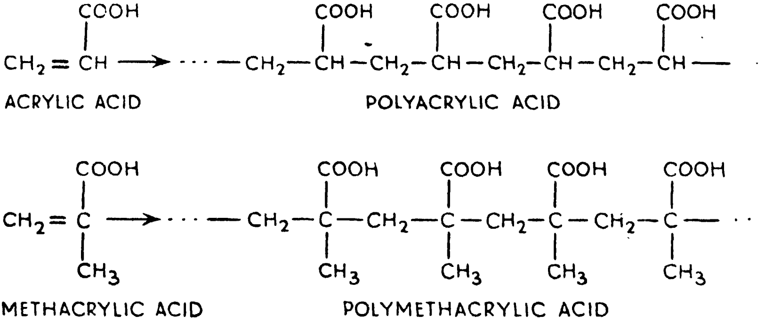
REFERENCES

1 Barron, Dean and Scott. *Trans. I.E.E.*, 1944, **91**, 297.
2 Fowles. *Wire and Wire Products*, 1943, **17**, 615.
3 Fortner. *India Rubber World*, 1948, **118**, 671.
4 Intemann. *Wire and Wire Products*, 1943, **17**, 618.
5 Veit. *British Plastics*, 1943, **15**, 353.
6 Photograph by courtesy of B.X. Plastics, Ltd.
7 ,, ,, *Plastics.*
8 ,, ,, Francis Shaw & Sons, Ltd.

CHAPTER XXIV

ACRYLIC RESINS AND METHACRYLIC RESINS

ACRYLIC resins are probably the most spectacular plastics at the present time. The best-known material in this country, "*Perspex*," has received unlimited publicity owing to its connection with aircraft. So much so, in fact, that the word is now a generic term for cockpits, astradomes and windows generally, in aeroplanes. The use for this application must run into many thousands of tons. The use in aircraft not only represents large areas of material of normal thickness, but also includes bullet-proof areas where the thickness may be considerable.



$$CH_2{=}CH(COOH) \longrightarrow \cdots -CH_2-CH(COOH)-CH_2-CH(COOH)-CH_2-CH(COOH)-CH_2-CH(COOH)- \cdots$$

$$CH_2{=}C(CH_3)(COOH) \longrightarrow \cdots -CH_2-C(CH_3)(COOH)-CH_2-C(CH_3)(COOH)-CH_2-C(CH_3)(COOH)-CH_2-C(CH_3)(COOH)- \cdots$$

Fig. 212

During the war the demand for aircraft was very large. Other uses have more than made good the much diminished demand in this field.

It must be realised that Perspex is merely one of a very large and growing family of materials. It is actually a polymer of methyl methacrylate, which is a chemical derivative out of the family of acrylic resins.

A closely related material, acrylic nitrile, is already a leading component in the production of some forms of synthetic rubber, notably Perbunan. As a consequence of this activity, large quantities of acrylic products should become available at comparatively low cost.

Acrylic resins are a very versatile group of materials, and their uses are spreading into many industries. They are available in numerous forms which obviously increases the scope. They range from hard, glass-like materials capable of replacing glass, to flexible rubbery products capable of replacing rubber.

The acrylic plastics are based on the esters of acrylic acid and methacrylic acid respectively. The possible chemical changes are obviously very great. By far the most important are the methyl and ethyl esters of acrylic acid and methacrylic acid and the copolymers which they readily form with each other. All the materials are thermoplastic, and the usual implications of this characteristic apply to them, that is to say, that when softened by temperature they may be compression moulded or injection moulded, extruded and generally manipulated.

Since the plastics are also commercially offered as aqueous dispersions, it is evident that they can be utilised in many ways.

The monomers are obtained as comparatively stable liquids and can thus readily be poured. They may be cast to any shape and are then easily polymerised to give hard, glass-like solids, etc. Every industrial country in the world is interested in their production, although most has been heard of them in Great Britain, in America, and in Germany.

In Great Britain the leading commercial materials of this type are: *Perspex*, which is polymerised methyl methacrylate, and *Diakon*, which is the material in the form of moulding powder. In America the Du Pont Company manufacture *Lucite*, both as sheet and moulding powder. The other American concern, Röhm & Haas, produce *Plexiglas* sheet and *Crystalite* powder. A firm of the same name produces similar materials in Germany. In the United States in 1943, 70 million pounds were used. In 1947, however, the amount used was about half the peak quantity.

Methyl Methacrylate Sheets. The manufacture of methyl methacrylate sheets is a major industrial activity in the U.S.A., in Germany, and in Great Britain. Most of the American output of 90 million pounds a year is in this form. German production had reached 10 million pounds a year. Thus German production was divided up into:

(*a*) Cast sheet, 90 per cent.
(*b*) Pearl polymethyl methacrylate for dental work, 10 per cent.
(*c*) Small tonnages of adhesives and finishes based on acrylic resins.

The Germans made three types of sheet, respectively:

1. Unplasticised polymethyl methacrylate.
2. Polymethyl methacrylate with 4 per cent dibutyl phthalate.
3. Copolymer of 91 parts methyl methacrylate, 7 parts n-butyl acrylate with 2 parts dibutyl phthalate.

Historical Angle. This class of materials has been known for a very long time, although the commercial application is of very recent date. As far back as 1843, Redtenbacher[19] prepared the ethyl ester of acrylic acid. Fittig[6] obtained a glassy polymer of ethyl methacrylate in 1877. In 1880 Kahlbaum[11] was able to prepare the transparent polymer of methyl acrylate. Shortly afterwards, in 1883, Weger[27] obtained the methyl, ethyl and propyl esters of acrylic acid. The preparation and study of numerous other derivatives, including acrylic acid amide, chloride and nitrile was carried out by Moureu.[14]

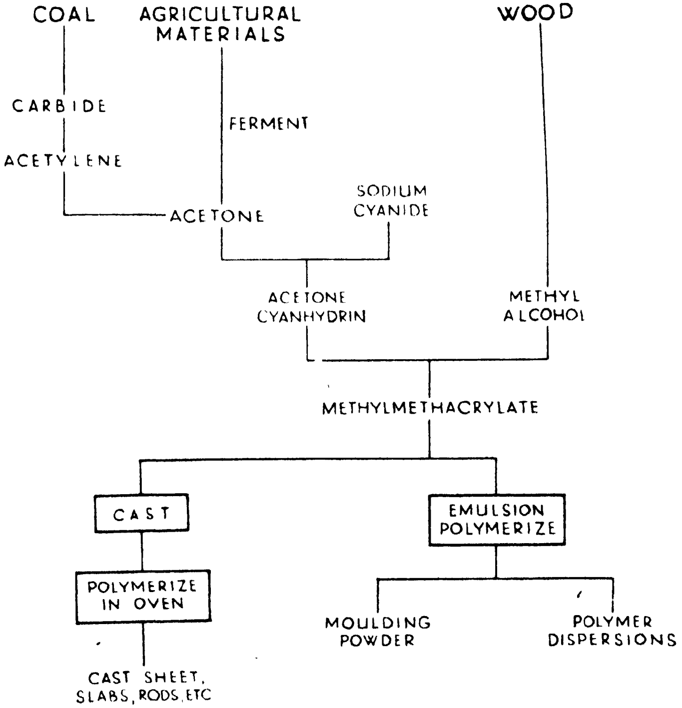


Fig. 213. Flow sheet for methyl methacrylate resins

The present-day uses of acrylic plastics can be regarded as based on the extensive work of Röhm[22] who, after numerous researches succeeded in 1901 in preparing solid transparent polymers of acrylic acid derivatives. However, nothing could be done with these materials at the time since there was no satisfactory method for obtaining the monomers on any reasonable scale. Consequently, commercial production did not commence until 1931. In this year, Bauer,[1] an associate of Röhm, developed successful methods for preparing acrylic esters. Röhm and Haas[23] also achieved a satisfactory process.

However, the use of cast methyl methacrylate resins in sheet form was exclusively a British development.

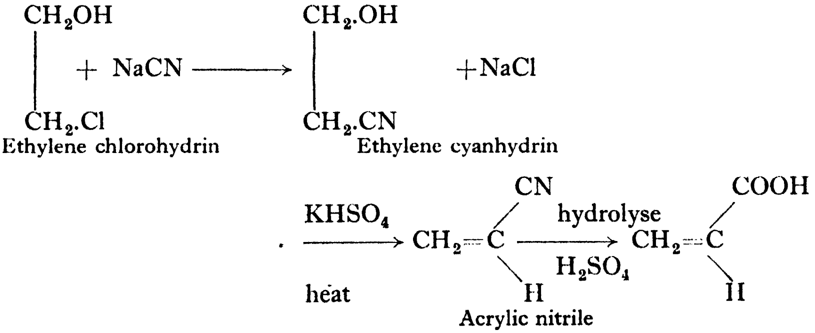
From 1930 onwards intensive work was carried out in Great Britain under the auspices of Imperial Chemical Industries Ltd., and the subject was carried well forward by Caress,[21] Crawford,[3] Gates, Hill,[9] Renfrew,[20] etc. The possibilities of the polymers were so attractive that production commenced from that time, and has expanded at a rapid rate. The expansion has, of course, been profoundly affected by the enormous demands imposed through the war-time expansion of aircraft industries all over the world.

Preparation of the Monomers. Up to the present time the main difficulty has been the preparation of monomers, which involves a series of complex chemical reactions. The result is that the plastics produced have been somewhat expensive and limited in application. This accounts for the high cost of products. Intensive work prompted by present-day necessities should find much more satisfactory methods. A much wider usage of these plastics will then take place.

Acrylic acid may be considered as a member of the vinyl family. It has the characteristic vinyl grouping, which no doubt is responsible for the ease with which it polymerises.

Chemical materials employed are ethylene and sodium cyanide for the acrylic esters, and acetone and sodium cyanide for the methacrylic esters. Acetone can of course be obtained from alcohol, from acetylene, or by fermentation processes from grain. Ethylene may be obtained from petroleum derivatives, from coal, or from alcohol. The chemical reactions are as follows.

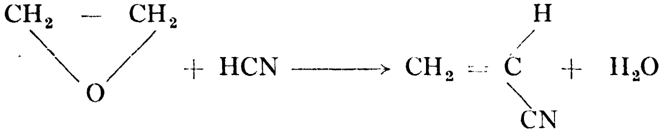
Acrylic Acid. The formation of acrylic acid esters conveniently starts from ethylene chlorohydrin. This is treated with sodium cyanide and yields ethylene cyanhydrin. When this is heated in the presence of sodium hydrogen sulphate, acrylic nitrile is formed, the most important derivative from the synthetic rubber angle.



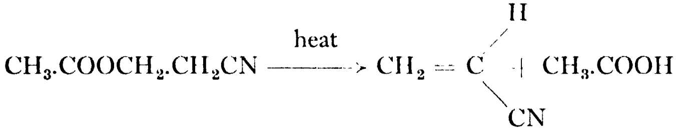
$$\begin{array}{l} CH_2OH \\ | \\ CH_2.Cl \end{array} + NaCN \longrightarrow \begin{array}{l} CH_2.OH \\ | \\ CH_2.CN \end{array} + NaCl$$

$$\xrightarrow[\text{heat}]{KHSO_4} CH_2{=}C(CN)H \xrightarrow[H_2SO_4]{\text{hydrolyse}} CH_2{=}C(COOH)H$$

Another method is the direct catalysed combination between ethylene oxide and hydrogen cyanide.



Another process proceeds according to the following reaction:



$$CH_3.COOCH_2.CH_2CN \xrightarrow{\text{heat}} CH_2 = \overset{H}{\underset{CN}{C}} + CH_3.COOH$$

Acrylic acid is a colourless liquid, boiling at 141° C., having an odour like acetic acid. Structurally it is similar to vinyl derivatives. It is itself capable of polymerisation to a solid, which, however, is not of particular interest.

Derivatives of Acrylic Acid. Acrylic acid can be esterified with numerous alcohols to give a wide variety of monomers. As the molecular length of the alcohol increases so do the properties of the ultimate polymers become more elastic; the softness, flexibility, heat resistance and water resistance also improve. The properties depend upon the chemical constitution of the monomer and the method employed for polymerisation.

Methyl acrylate and ethyl acrylate, etc., are colourless liquids, which may easily be polymerised to transparent solids. They are insoluble in water and in alcohol, but dissolve in acetone, benzene, and chloroform.

The polymerising conditions largely control the nature of the final product. These may range from hard, tough, thermoplastic materials to rubbery products, down to semi-fluids. Thus the polymer of methyl acrylate is a tough, pliable, rubber-like substance, films of which may be stretched more than 1,000 per cent. The polymers of ethyl acrylate are softer and more elastic. Many of the butyl acrylate polymers are rubbery, but much softer and inclined to be tacky.

The group includes not only the organic esters but also halides, nitriles, etc., although none of these have attained any commercial importance as polymers.

Acrylic nitrile is a colourless liquid boiling at 77° C. and possessing a mild, pleasant odour. It polymerises to a hard, white powder.

Acrylic acid can, of course, be obtained in the laboratory by oxidation of the corresponding alcohol aldehyde, i.e. acrolein by air or by means of oxidising agent.

Methyl Methacrylate. Methyl methacrylate is derived from acetone, which, of course, can be obtained from acetylene. Acetone reacts with hydrogen cyanide to give acetone cyanhydrin. This is treated with sulphuric acid and methyl alcohol.

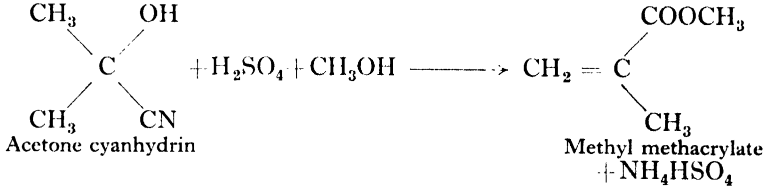


Fig. 214. Vessels in which methyl methacrylate syrup is prepared for the manufacture of "Perspex"[29]

Production of Methyl Methacrylate Monomer. The process is carried out in four stages: Acetone cyanhydrin is added to 100 per cent sulphuric acid. A lead-lined vessel fitted with a stirrer and water-jacketed is used. The charge is:

240 litres	Acetone cyanhydrin
195 litres	Sulphuric acid
0·5 kg.	Tannin

Tannin is the inhibitor of polymerisation. It is dissolved in the acid, and the cyanhydrin is run in during 30 minutes, temperature being held at 80° C.

The second stage is conversion to methacrylamide sulphate. The mixture is transferred to another vessel and maintained at 125° C. for 20 minutes. It is then cooled to 90° C.

Stage three is the conversion to methyl methacrylate. 840 kg. methanol, 400 kg. water and 0·5 kg. tannin are placed in a tiled, steel cylinder, fitted with stirrer. Six batches from the previous stage are added, maintaining temperature at 92° C., taking about three hours.

The final stage is the steam-distillation of methyl methacrylate. A series of washings and distillations brings the purity up to 99·9 per cent. The yield is 80–85 per cent of the cyanhydrin used.

Methyl methacrylate is a colourless liquid with a specific gravity at 16° C. of 0·9497 and refractive index n_D^{16} 1·4168. It boils at 100·3° C. It is soluble in most organic solvents, but is insoluble in water. The viscosity at 25° C. is 0·59.

It is interesting to learn that "Plexiglas" in Germany was made by this process under licence from I.C.I. Ltd.

Methacrylic acid derivatives yield polymers which are much harder than the corresponding acrylic acid derivatives, only becoming soft when the amyl esters are formed. They all share certain common properties; thus they are all thermoplastic, very transparent, resistant to ageing, sunlight or oxygen, and very resistant to chemical attack. They have excellent adhesive properties and are not affected by oils, petrols, or solvents.

Polymerisation. Acrylic esters and methacrylic esters are in general free-flowing liquids which are quite easy to handle and they polymerise very readily. The process is assisted by heat, light, ozone and oxygen. A variety of oxidising agents, such as hydrogen peroxide, benzoyl peroxide, etc., are excellent catalysts. The reaction can be inhibited by adding materials such as hydroquinone. The presence of oxygen appears to be necessary for polymerisation to take place. Certainly it must be present in order to carry polymerisation forward with any rapidity.

As the molecular length of the molecule increases so the properties of the polymers change. They become more elastic; the softness, flexibility, heat resistance, and water resistance also improving. These properties depend not only upon the chemical constitution of the monomer, but also to some extent on the method employed for polymerisation.

The pure monomers are stable liquids which can be stored for months without polymerisation and handled without difficulty. Any tendency for autocatalysis which is found with methyl methacrylate may be inhibited by a similar method to that used for styrene, i.e. the addition of small quantities of anti-oxidants. Hydroquinone or pyrogallol are typical inhibitors used in amounts up to 1 per cent.

Casting Methyl Methacrylate Sheets. Monomer containing 3·64 per cent dibutyl phthalate as plasticiser is thickened by beating in a stainless steel vessel with 0·02 per cent benzoyl peroxide. It is boiled for about 10 minutes.

Fig. 215. Some of the polymerisation ovens[29]

Plate glass cells are used for casting. The glass is $\frac{1}{8}$ inch thick. The two sheets of plate glass forming the cell are separated by the desired distance (thickness) by strips of laminated phenolic. The edges are sealed by means of strong paper. Before filling with the syrup, the laminated distance pieces are removed. The syrup is run in and air bubbles are allowed to escape. The sealed moulds are then heated in ovens:

1st oven	at 55° C.	for 8 hours
2nd oven	at 50–62° C.	for 10 hours
3rd oven	at 85–125° C.	for 8 hours

Acrylic acid nitrile, chloride, amide, etc., also polymerise, but no outstanding commercial applications have appeared for them. These are employed as accessories in copolymerised materials. The outstanding example is, of course, acrylic nitrile, which is used to the extent of 25 per cent with butadiene to make Perbunan, Hycar, and other synthetic rubbers.

The process may be carried out by a number of procedures. In the first place, straightforward heating of the liquid monomer converts them into the solid, transparent polymer in due course. As a consequence, this makes the process of casting quite practicable, and indeed this is widely practised. Another procedure is to dissolve the monomer in a suitable solvent and to polymerise in this condition. It is found in many cases the polymer is insoluble in the original solvent, and as it is formed it comes out of the solution, so that this provides a ready method of obtaining the polymer in an easily separated condition and finely divided.

TABLE 134

POLYMERS OF ETHYL ACRYLATE

Molecular Weight	Degree of Polymerisation	Properties of Polymers
2,200	22	A viscous oil.
7,800	78	Tough fluid mass.
41,500	145	Tougher than previous polymer.
14,000	410	Very tough. Non-flowable.
175,000	1,750	Tough, elastic rubberlike mass.

Ethyl acrylate polymerised in these conditions comes out as a coherent porous powder, while methyl methacrylate comes out as a voluminous powder. Acrylic acids are generally polymerised in paraffin hydrocarbons, which have a selective effect. The specific gravity of the solvent plays a part in determining the particle size. In a normal way the monomer concentration may be up to 40 per cent. The usual catalysts are employed in this procedure. This method was first developed by Bauer and Lauth.[2]

Acrylic ester polymers are largely prepared by the process of emulsion polymerisation. In this the liquid monomer is formed into a stable emulsion in water by shaking with an emulsifying agent. Catalysts are present and heating is carried out. The process may be kept under control by addition of cold water. The emulsion gradually changes in character, becoming a dispersion of polymer particles which may be separated quite easily. Variations of this procedure result in the formation of stable latices, which have acquired a wide commercial field. They may be coagulated by the addition of acids or polyvalent salts. These products are completely miscible with rubber latex and have been widely used. These emulsions were first described by Bauer in 1931.[10]

The characteristics of a given polymer are markedly affected by variations in the conditions of polymerisation, such as changes in temperature, time, solvent, and type and amount of catalyst. These variations control the particle size of the final product. As would be expected, the lower polymers are characterised by lower viscosities, lower tensile strength, and generally poorer film-forming characteristics.

The properties of the resin depend on both the chemical composition and the conditions of polymerisation. Methacrylates are much harder than the corresponding acrylate resins. The methacrylates produce harder, tougher, but less elastic films than do the acrylates. The same is true for the methyl ester as compared to the ethyl ester of a given acid.

The order of hardness is thus:

Methyl methacrylate—hardest
Ethyl methacrylate
Methyl acrylate
Ethyl acrylate—softest

Properties of Methyl Methacrylate Polymers. Methyl methacrylate can be cast to any desired shape in suitable moulds and then polymerised by simple heating. Sheets and slabs of all sizes are made in this manner. Rods and tubes may also be prepared by casting. Rods may also be machined from solid cast slabs.

TABLE 135

MECHANICAL PROPERTIES OF METHYL METHACRYLATE POLYMER

Specific gravity	1·19
Tensile strength, lb./sq. in.	5,000–9,000
Elongation, %	3
Modulus of elasticity, lb./sq. in. × 10^5	5
Impact strength, Izod (notched), ft./lb. per inch	0·3
Brinell hardness	17
Compression strength, lb./sq. in.	11,000
Shrinkage, inch per inch	0·004

Monomeric esters of methacrylic acid have low viscosities and are well suited as impregnating agents which can be polymerised. Many porous materials have been treated with methyl methacrylate which has then been polymerised by heating. In this way products have been made with improved resistance towards water, oil, alcohol, acid, and alkali. Methyl methacrylate monomer can impregnate wood, which when heated will yield a final product containing as much as 60 per cent by weight of resin.

Methyl methacrylate polymers are soluble in esters, in acetone and other ketones, in aromatic hydrocarbons such as benzene and toluene, etc., in chlorinated hydrocarbons (except carbon tetrachloride), and in concentrated organic acids such as glacial acetic acid. They are not soluble in water, glycerine, aliphatic alcohols, aliphatic hydrocarbons. They are impervious to all but the strongest mineral acids and alkalis. They are resistant towards vegetable oils, greases, etc.

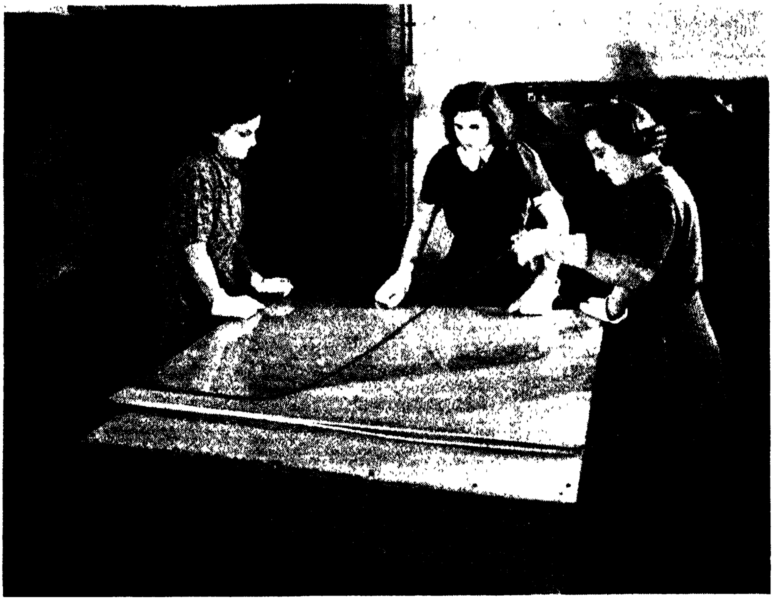


Fig. 216. A sheet of "Perspex" after the heat treatment[29]

Methyl methacrylate polymer has most exceptional clarity, which is its outstanding characteristic. Light transmission of 92 per cent is superior to anything else known at the present time. It has the relatively high softening temperature of 80° C., high tensile strength, and good impact strength.

It is completely light-stable and has satisfactory dielectric characteristics. One of its most valuable attributes is the low specific gravity, so that sheets or shaped articles are almost one-third the weight of glass. This is obviously of the utmost importance to aircraft. The impact strength is ten times as high as that of glass.

Apart from these inherent properties, the material can be moulded easily either by compression or by injection methods. Moreover, the mouldings or the castings can be readily worked. The material can be machined in almost any manner, either sawn, cut, turned, drilled, formed, blanked or swaged. It can be ground, polished, sanded or routed to give almost any desired shape or effect. For general purposes where it is designed to take the place of glass it suffers from the disadvantage of being much softer than glass. Thus it scratches readily, although a scratched surface can be restored by polishing without any great difficulty.

TABLE 136

ELECTRICAL PROPERTIES OF METHYL METHACRYLATE

Surface resistivity at 20° C. and 75% humidity, ohms	$>10^{16}$
Volume resistivity at 20° C. and 75% humidity, ohm/cm.	$>10^{15}$
Breakdown voltage at 20° C. and 75% humidity on ⅛-inch thick specimen, volts/mil.	280–300
Permittivity at 20° C. and 75% humidity at $5<10^7$ cycles	2·6
10^6 cycles	2·9
800 cycles	3·6
50 cycles	4·0
Power factor at 20° C. and 75% humidity at 5×10^7 cycles	0·022
10^6 cycles	0·019
800 cycles	0·033
50 cycles	0·038

Like polystyrene, polymerised methacrylate when heated strongly regenerates the monomer, and it is said that 90 per cent recovery is possible by this procedure. According to Strain,[25] at 450° C. nearly 90 per cent of monomer may be obtained. At 250° C. decomposition is quite small.

The dielectric properties of methyl methacrylate resin make it of value in the electrical insulation and instrument field. Here again the transparency, non-tracking qualities, inertness to ozone, high softening temperature, strength, water, oil, and chemical resistance, and the decrease of power factor with increase in temperature, combine to make the material very attractive. It is also slow-burning. It is used for making coil supports, etc.

Depolymerisation of Scrap Methyl Methacrylate Resins. Scrap methacrylate resin which accumulates during manufacture and shaping may be reconverted to monomer by thermal depolymerisation. The German procedure was as follows:[31]

The scrap is broken up into pieces approximately ¾ to 1 in. mesh. This is the form used for depolymerisation.

The depolymerisation reactor consists of a steel tube of length approximately 2½ meters and average diameter 30 cm. A conveyor screw passes down its length. The tube is of slightly oval cross-section, to allow of escape of vapours past the screw. This tube is heated by electricity. At one end the scrap is fed into the reactor from a hopper by means of another screw conveyor. At the other end of the reactor are a vapour rise pipe leading to a condenser, and a downfall pipe leading to a water-sealed trough. The whole apparatus is made of steel; the reactor tube is made of heat-resistant steel. The operating temperature of the reactor varies along its length between 380° and 400° C.

The scrap which is fed into the reactor is moved along it by the screw, undergoing depolymerisation meanwhile. Depolymerisation is largely complete; non-volatile appearing at the end of the screw conveyor consists of a little carbon, with at time some still undepolymerised material. Water runs through the trough into which the non-volatile material falls. The carbon is carried away by the water, the undepolymerised material remains in the trough, from which it is removed from time to time and returned to the scrap hopper.

The vapours passing out of the reactor via the riser pipe are condensed. The condenser is connected to a large water vacuum pump, which carries away under slightly reduced pressure the unpleasant smelling gases evolved in the process. The methyl methacrylate is redistilled.

The monomer is sufficiently fluid to impregnate tightly wound electrical coils, following which the resin can be polymerised to give a component from which no solvent remains to be expelled. The fluidity of the monomer permits this rapid impregnation. Solutions of the polymer can be used also for the impregnation of coils, particularly where complete sealing is not necessary. Rotors and armatures can be dipped in resin solutions to bond the wires firmly in place. The toughness and strength of methyl methacrylate resin are of great significance in such applications.

The Production of Tubes and Rods. The manufacture of tubes, rods, and other sections of methyl methacrylate is likely to attain great importance. Already such productions have shown great possibilities in many directions. Methyl methacrylate monomer is heated in a container to bring about partial polymerisation. It becomes a thick viscous liquid and is handled in this condition. About 1 per cent of a suitable catalyst is thoroughly mixed into the liquid which is then run into multiple moulds. These are then gradually heated in a hot water bath and the material polymerises to its final hardness after which it is ejected. When highly polished moulds are used, highly polished brilliant transparent products are obtained in this manner.

Tubes may be prepared by centrifugal casting. Up to the present time polymerisation of large volumes of monomer has not proved very easy. This is due to the fact that the process assumes a violent, almost explosive course. Polymerisation is very exothermic, heat of the order of 20 calories per mol is developed, leading to a very high temperature build-up.

Optical Characteristics of Methyl Methacrylate Resins. The methyl methacrylate type of material has far better light transmission than glass. Glass does not allow all the light to pass through, and the thicker the glass the less the passage of light, thus it is difficult to see any object through glass which is more than six inches thick. On the other hand, articles seen through slabs of methyl methacrylate three feet thick are as clear as if no obstacles were intervening. Moreover, thick sections of the material, although transparent, are as resistant to shock as armour plate. For example, a sheet is ten times as strong as glass of equal thickness, and is very difficult to break. The toughness and flexibility add to this superiority.

When methyl methacrylate resin does break, large pieces are formed without cutting edges. This has opened up great possibilities for its application as substitute for glass. The greatest field until recently has been in place of glass for aircraft. It is used in aircraft manufacture for cockpits, turrets, bomber noses, and in other parts where visibility is required. In fact, during the war the requirements of aircraft limited very acutely any other applications for this class of material. Of course, a contributory factor for aircraft, apart from these characteristics, is the lightness, for having a specific gravity of 1·19, methyl methacrylate polymer is one of the lightest plastics; this is almost one-third the weight of glass and represents an enormous saving in weight.

Methyl methacrylate gauges and inspection windows are widely used for many military and other instruments. They can be quickly produced in large quantities with great efficiency. They stand rough treatment without injury and reduce breakages due to careless installation.

Other applications include the use for shipping purposes, and also for bullet-proof glass in various military vehicles. It seems highly probable that one activity may be the application of these materials to motor-cars to give complete visibility without any obstructions such as exist at the present time.

Another leading factor in the use as sheet is the fact that such sheets can be cast, which is an easy technique, and the production does not involve undue difficulties.

Other characteristics which add to their merits for exposed conditions such as in aircraft, include the facts that not only are the materials very rigid, but they show no dimensional changes when subjected to the variations in humidity and temperatures experienced throughout the world. They are highly resistant to moisture over a very wide range of temperature.

Another outstanding feature is the ability of these materials to conduct light round corners, the property known as piping light. This has opened up a very wide field of application, including their use for surgical instruments, and in completely different fields for display and advertising purposes. Another useful characteristic is the fact that they show edge-lighting effects.

Handling of Methacrylate Sheet Material. Methacrylate plastic is prepared as a cast sheet on a very large scale. The primary use of such sheet is for aircraft purposes, the leading type in this country being Perspex. It is widely employed for domestic ware, fancy goods, display stands, advertising articles, etc. It is also used in thick sections as bullet-proof glazing for military vehicles, etc. It is available in sheets of varying thicknesses ranging from one-eighth of an inch up to an inch or more.

The use of flat sheets of methacrylate resins does not present many difficulties. The only precautions necessary are to avoid contaminating the surface. In any event, these are generally protected by adhesive masking paper.

The preparation of small, flat articles is merely a question of cutting out or stamping out from cold material. Discs for lenses, display articles, and so on, are easy to make. Cut sections can be cemented together to form fabricated articles.

There is a great deal of activity in the preparation of shaped and curved products based on this material, for being thermoplastic, it can be softened, shaped and allowed to set once again.

Sheets of methacrylate resin when suitably softened may be stretched over forms, and this technique is practised for quite large products. In this case a number of operatives stretch the sheet over the form, the ends being held down by suitable clamps. Methods along these lines are being widely employed for making a variety of curved sections such as bomber noses, astradomes and the like. Manipulation of sheet into curved forms is now a very large industry.

The primary consideration in handling sheet material is to prevent dirt or other marks which may affect clarity. Particularly when in a heated plastic condition the material tends to mark very easily. The sheets become thermoplastic at temperatures above 100° C. When soft the plastic can be bent or formed to any shape. Material set in this

TABLE 137

PROPERTIES OF TRANSPARENT ENCLOSURE MATERIALS

Property	Methyl methacrylate	Cellulose acetate	Ethyl cellulose	Cellulose nitrate	Plate glass
1. Tensile strength, p.s.i. . . .	5,000–7,500	4,000–11,000	7,000–9,000	6,000–9,000	6,500–30,000
2. Compressive strength, p.s.i. . .	10,000–15,000	4,000–30,000	10,000–12,000	20,000–30,000	36,000
3. Coefficient of linear expansion per deg. F × 10^{-5}	3·9–5·0	8–9	5–8	6·5–8·9	0·33
4. Index of refraction	1·49–1·51	1·49–1·50	1·47	1·50	1·52
5. Light transmission, % . . .	90–92	85–92	91	90°	88–91
6. Specific gravity	1·18–1·20	1·27–1·37	1·08–1·18	1·33–1·60	2·5
7. Burning rate, $\frac{1}{8}$-in. sheet, in 1 min. .	1·1	1·5–2·0	Slow	Highly inflammable	None
8. Solubility	Soluble in esters, ketones and aromatic hydrocarbons		Generally soluble in organic solvents except hydrocarbons		Insoluble
9. Effect of age	Practically None	Slight shrinkage	Slight	Hardens slightly	None
10. Effect of sunlight	Practically none	Slight discoloration	Slight	Yellows and embrittles	None

manner will tend to revert to its original flat shape when warmed to the softening temperature.

In the normal way the sheets are heated in hot-air ovens, being hung vertically. Other methods can be used. The sheets are softened by immersion in boiling water. Another alternative is immersion in hot, vertically. Other methods can be used. The sheets can be softened by clean oil.

Latterly, it has been found that radiant heat is a very convenient clean method for softening methacrylate resin sheets. With this method it is generally only necessary to heat the material for a minute or two before it becomes soft. It is then similar to soft rubber, when it can be readily bent and stretched without much force.

In the usual way forms may be made of most of the ordinary materials such as wood, plaster, or metal. There are no special mechanical requirements, since no great forces are applied. Obviously, the surfaces should be smooth, and they must be covered with cloth or some other suitable material to protect the methacrylate surface. Dimensions of the formers should be such as to allow for shrinkage of the plastic and also sufficient excesses for trimming edges and the like. In making shapes the sheet is finally held down by means of a suitably formed yoke or ring. The formed products must be allowed to chill completely before being moved. Fairly wide tolerances must be allowed of the order of 0·15 inches on deep drawn curves, one-eighth of the radius on internal curves, etc.

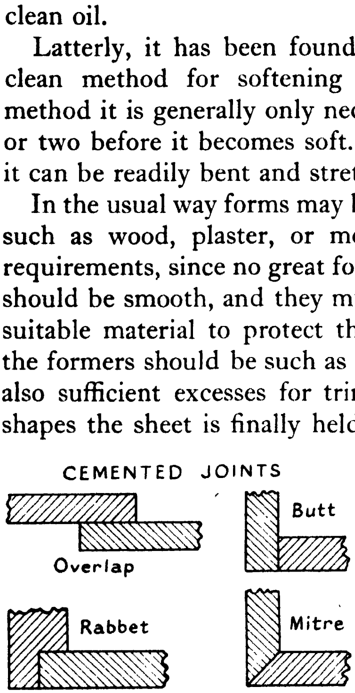


Fig. 217. Typical Joins made with methyl methacrylate resin sections

Cementing Methacrylic Resins. When repairs may be necessary then acetone, glacial acetic acid, ethylene dichloride and lacquer thinners will serve to soften the surface so that a satisfactory bond between the patch and the original section may be obtained. By dissolving a few chips of the polymer in ethylene dichloride, glacial acetic acid or monomeric methyl methacrylate, a good, viscous cement may be obtained. Methylene chloride is perhaps the best solvent for cementing "Perspex" pieces together.

It is often necessary to join methacrylate sheets or components. This is a task of some difficulty when transparency must be maintained. Preparation of the surfaces is obviously a prime consideration. Surfaces should preferably be machined. The use of solutions of methyl methacrylate polymer in ordinary solvents is practicable. But while the immediate effect is satisfactory the adjoining surfaces rapidly craze and lose transparency.

Two methods are widely practised. One method involves the use of monomeric methyl methacrylate, to which a small amount of catalyst, e.g. 1 per cent of benzoyl peroxide, is added prior to use. The parts to be joined are soaked in this for an hour. They become soft, are then fitted together and clamped until set.

The second method involves using a solution of polymethyl methacrylate in glacial acetic acid. The parts are softened with this solution and then pressed together. The joint is firm within two hours and may be machined after twenty-four hours. In each instance the use of warm solutions, below 60° C., hastens softening of the polymer.

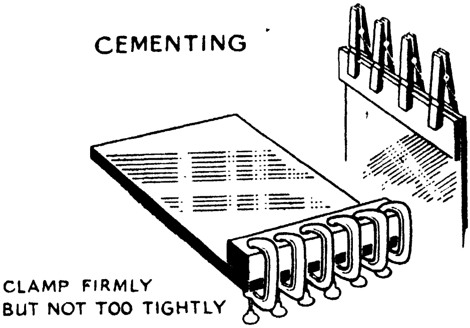


Fig. 218. Method of clamping methyl methacrylate sections being joined

For cementing polymethyl methacrylate to textiles, paper, etc., the following has been extensively used in Germany: 5 per cent polymethyl methacrylate in a mixed solvent comprising 63·25 parts methylene chloride, 26·25 ethylene chlorhydrin, 10·5 xylene.

Moulding Methacrylic Resins. Putting aside the transparent sheet aspect one comes into the field of moulding. The methacrylic resins are available as moulding powder or granules of various grades. These are prepared by polymerising the monomer in aqueous dispersion under suitable conditions. Small proportions of plasticiser such as dibutyl phthalate may be added.

Alternatively methyl methacrylate powder may be rendered plastic on hot mixing rolls and the plasticisers and dyestuffs may be added. The mass is finally reduced to moulding granules by mechanical disintegrators.

Gates and Renfrew[7] obtained granular polymerised dispersions of esters of acrylic and methacrylic acids, or mixtures, by polymerising aqueous dispersions of the monomers in the presence of calcium, barium, or magnesium persulphates.

They may be compression moulded, the only precautions necessary being that mouldings must be chilled before ejection since the materials are thermoplastic. Inserts and threads can readily be incorporated as part of the moulding operation.

Most moulding is, however, carried out by the injection process, the temperature conditions involved being between 160° C. and 220° C. By virtue of the transparency it is evident that a complete colour range is available in every shade and tone with extremely attractive effects. As a consequence a whole range of attractive decorative articles have been prepared, such as cosmetic containers, fancy goods, jewellery, etc.

One very interesting moulding application which shows great promise follows directly from the excellent optical characteristics. These correspond to those obtained with the cast material. It is the mass production of lenses and other optical accessories. This development is expanding rapidly, and extremely satisfactory results are being obtained. Such lenses in general are used where scratching is not likely to be encountered. They are in great demand for instruments of every description, for war equipment, ships, aircraft, etc. One interesting development of this is the production of spectacle lenses and of contact lenses. Another development in the same field is, of course, the moulding of these materials for clock glasses, indicator dials, and transparent covers.

With the end of the war it became possible to apply the material to much wider applications, such as salad bowls, utensils, compacts, trays, kitchen sinks, bathroom equipment, wind-shields, port-holes, etc.

In general, positive moulds are used for compression moulding, i.e. the entire pressure is applied to the material. The conditions for the production of satisfactory mouldings, especially when transparent, must be carefully studied. For example, the technique recommended for "Diakon" moulding powder is as follows:

The mould should be heated to about 50° C., and the moulding cycle carried out as follows:

(*a*) While continuing to heat the mould, fill it with slightly more powder than the weight of the finished moulding.

(*b*) Close the mould under low pressure of about ½ ton per sq. inch. The actual pressure to be used varies with different moulds, but must not be enough to cause the male and female portions of the mould to meet while heat is still being applied, or imperfect mouldings will result.

(*c*) Continue to heat the mould (while still under low pressure) to a temperature of 150° C. to 190° C., for "Diakon" F, and 130° C. to 180° C., for "Diakon" D. Insufficient heating (both in temperature and time) prevents the material from becoming plastic enough to take up the contours of the mould.

(*d*) Begin the cooling process immediately by shutting off the steam heating and circulating the cooling water. No cure time is needed.

(*e*) Raise the pressure to 1–2 tons per sq. inch on the moulding and maintain this higher pressure until the temperature of the mould is again down to about 50° C. This pressure must be maintained if sink marks, voids, or other defects are to be avoided.

(*f*) Release the pressure, open the mould and eject the moulding. This completes the moulding cycle and the mould is ready to receive its fresh charge of powder.

German Granular Moulding Powders. "Plexigum" is the name given to the German granular or pearl polymers. There are several types:

(*a*) Injection moulding powder, comprising 92 per cent methyl methacrylate, 6 per cent methyl acrylate, 2 per cent cetyl alcohol (lubricant).
Molecular weight is about 60,000.

(*b*) Pure methyl methacrylate.
Molecular weight, 75,000.

(*c*) Fine particles for dental purposes.
Molecular weight, 100,000.

They are made in the following manner. The reaction mixture comprises:

1 part monomer (plus catalyst).
2 parts aqueous suspension of magnesium carbonate

18 grammes $MgCO_3$ per litre gives very fine pearls or granules. Twice this amount gives the standard moulding granules. 0·275 per cent benzoyl peroxide as catalyst gives a product with molecular weight 75,000.

Actual polymerisation is done in glass-lined pressure vessels fitted with stirrers. Polymerisation time is 1 hour at 120° C. The product is washed with dilute sulphuric acid to remove magnesium carbonate, then with water, being finally dried.

Fabrication of Methacrylate Mouldings. Owing to the fact that transparency is the outstanding feature of methacrylate articles, it is important that fabricating processes should not spoil this feature. It is necessary to use the right conditions for machine-drilling, and so on. For example, in handling such mouldings, the following drill conditions are emphasised.

TABLE 138

PROPERTIES OF MOULDED "DIAKON"

GENERAL PROPERTIES AT 20° C.

Property	Transparent Clear "Diakon"	
	D Medium softening for compression or injection	F High softening for compression or injection
Specific gravity (moulded)	1·19	1·19
Bulk density of powder . . .	0·7	0·7
Bulk factor of powder . . .	1·7	1·7
Water absorption (7 days' immersion of specimen 50 mm. diam. by 10 mm. thick), % by weight . . .	0·20–0·30	0·24–0·30
Heat resistance, °C. (Martens test) .	40–45	55–60
B.S.I. Grade temperature . . .	30° C. (Grade VI)	70°C. (Grade IV)
MECHANICAL PROPERTIES AT 20°C.		
Tensile strength, lb./sq. inch . .	7,500–8,200	8,200–10,000
Impact strength (as B.S.S. 771), ft./lb. .	0·25–·030	0·30–0·35
Ultimate fibre strength in bend, lb./sq. inch	11,000–12,500	11,000–14,000
Brinell hardness	14–17	19–21

Drill design is extremely important. The most suitable drill should be made of high-speed steel or an equivalent material. The drill should have polished flutes, and the drill angles must be carefully studied.

A suitable polish for methyl methacrylate products is:

20 parts	Montan Wax
10 parts	Kieselguhr
1 part	Kaolin
69 parts	Decalin

Optical Applications of Methacrylic Resins. Among the transparent resins, polymethyl methacrylate possesses the most suitable properties for optical uses. The specific gravity of 1·19 is extremely low and compares with 2·3 for spectacle crown glass, and the refractive index number of 1·495 compares with 1·523 for glass. The outstanding property of the material is its exceptional transparency to the whole of the visible spectrum, throughout which the absorption of the material is negligible. It has a transparency to white light of over 95 per cent.

The chief objection to its use in optics was the inferior hardness as compared with glass. Methods for overcoming this are being developed. One process applies a fine film of silica to the surface.

It is an extraordinary coincidence that ratio of the refractive indices of polystyrene and polymethyl methacrylate corresponds exactly to the ratio between crown glass and flint glass. This means that special optical lenses can be made by using only synthetic materials.

It is also superior to white glass in transmission of the near ultra-violet radiations (approximately 60 per cent at $300\mu\mu$. where glass becomes opaque) comparing with special glasses evolved for ultra-violet transmission. It commences to absorb the infra-red radiations at wave-lengths of over $100\mu\mu$, becoming opaque to those over about $2,500\mu\mu$. Polymethyl methacrylate is a pure synthetic product and is capable of close control so that every product possesses the same identical physical and chemical properties. The dimensional stability of the material under extremes of atmospheric conditions is of considerable importance for optical purposes. It will withstand temperatures as high as 50° C. for many hours without visible change, and low temperatures actually increase the strength of the material. A further important point is that it is not liable to discolour or exhibit surface-crazing with age. Water absorption of the material is low and condensation upon the surface clears more rapidly than from glass. As has been shown, resistance to chemical attack is outstanding. It is not affected by perspiration and will not set up any form of dermatitis when in contact with the most sensitive skins.

Methacrylic Resins for Optical Lenses. A number of different methods of forming lenses from acrylic resins have been proposed. The powdered resin has been moulded into a solid mass of the approximate size and shape of the lens required, and finally ground and polished to the exact shape. Another technique is to cut blanks of the approximate size from large sheets or rods of the transparent resin, thereafter polishing and grinding the blanks. Care must be taken to avoid development of internal strains in the sheets or rods. Attempts have been made to dispense with the grinding and polishing operation by moulding the blank between two heated discs of polished glass (or very hard polished metal) which have been ground (in reverse) to the required dioptric surface. The edges of the blank are left unconfined in this procedure to allow expansion under pressure without causing any change in the shape impressed by the dies. While still warm the finished lenses were removed from the mould and hardened by sudden chilling at a very low temperature (-75°C.). According to one patent,[17] when using glass or quartz moulds for the direct shaping of lenses, the danger of cracking the mould can be reduced by applying compression only at the moment when the material in the mould reaches maximum plasticity, and by interposing a layer of gypsum between the metal support of the mould and the mould itself, so as to distribute the pressure more uniformly.

Most of the transparent resins have a refractive index of the order of 1·5. Polymethyl methacrylate has an index of 1·49, while that of polystyrene is 1·59.

The ratio of the two refractive indices is identical to that between the two leading optical glasses so that complex lenses offer no optical difficulties.

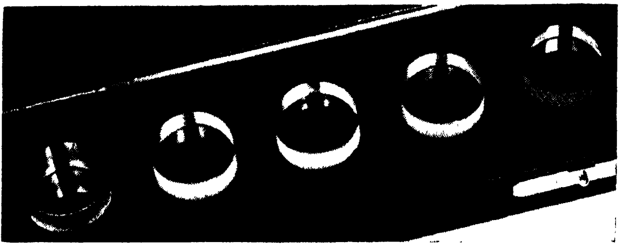


Fig. 219. Typical moulded lenses

It has recently been found that exceptionally high refractive indices are possessed by resins formed by polymerising the methacrylic esters of certain polynuclear phenols.[8] For example, ortho-hydroxydiphenyl methacrylate polymer has a refractive index in the vicinity of 1·618 The monomer is made by reacting ortho-hydroxydiphenyl (more commonly known as ortho-phenyl) with methacrylic anhydride in presence of pyridine and a polymerisation inhibitor, such as copper methacrylate. It has a very high boiling point and undergoes polymerisation in the usual manner in presence of benzoyl peroxide.

Optical resins with refractive indices intermediate between the above resin and polymethyl methacrylate can be obtained by copolymerisation, e.g. using a mixture of 40 per cent (by volume) methyl methacrylate, 40 per cent ortho-hydroxydiphenyl methacrylate, and 20 per cent acrylic acid.

Piping Cold Light. Methyl methacrylate resins and some other acrylic resins are able to carry light round curves; in effect, they are able to act as solid pipes for light. Rods having any degree of curvature, and of considerable length, show this effect. This action is so effective that rods of methyl methacrylate plastic, even when tied into complex knots, will transmit light perfectly. An object or picture at one end is clearly visible at the other. The explanation is that the high refractive index of the material is coupled with considerable internal reflection from the highly polished end surfaces. There is very little loss of light, so long as the wall is kept polished, and not roughened.

Needless to say, this is a property of the greatest significance. Polystyrene also shows this effect in a lesser measure, but polystyrene has disadvantages, e.g. its brittleness, which detract from the value of this characteristic. Glass and quartz are also able to transmit light round corners, but physical and technical disadvantages limit their value in this respect. They are difficult to fabricate; glass breaks easily; quartz, in particular, is awkward to handle, and is not available in large sections.

Methyl methacrylate resins, on the other hand, have all the advantages of toughness, resilience, and strength. Being synthetic materials, they are obtainable in sections of any shape and size. They may be cast or moulded to any shape, the processes lending themselves to mass production. Moreover, they are very easily fabricated.

There are many industrial outlets for which this property is of great significance. There are many locations which require to be illuminated, but which are ordinarily inaccessible.

One outstanding field of application making use of this curved light effect is in surgery and dentistry. Many complex surgical and dental instruments now make use of methacrylic resins.

Advantage of Cold Curved Light Instruments. Since light itself is of fundamental importance in surgical operation, methyl methacrylate resin may become one of the most important tools in the hands of the surgeon. Some of the more evident advantages of the material are:

1. Since this resin is a non-conductor of heat, and since the source of light is at a distance from the point of emission, the light remains "cold," however long the instrument is in use. In addition to many other reasons, an ordinary electric light bulb cannot be introduced into the body because of the heat evolved and the danger of explosion from ether flames.
2. There is no glare reflected back into the eye.
3. Because of the excellent electrical insulating properties of methyl methacrylate resin, there is no danger of electrical shock to the patient, and diathermy may be applied *in situ*.
4. The combination of light and instrument is unique in making surgical work completely independent of normal exterior sources of light capable of being destroyed or accidentally cut off.

5. Since the instrument can be made in curved form and in very complicated shapes, the illumination of deep-lying structures within the body, at the exact point where light is needed, becomes practicable.

Until comparatively recently one great difficulty was the inability of such instruments to stand up to sterilising conditions, i.e. immersion in boiling water. This trouble has now been largely overcome.

Heat-Resisting Methyl Methacrylate. In common with most thermoplastics almost the outstanding disadvantage of methyl methacrylate is the low softening temperature. This becomes a serious defect when the material is used for such purposes as surgical instruments where sterilisation in steam is involved. As a result of much research work new heat-resisting types have been evolved. Thus standard material when immersed in boiling water for 10 minutes showed a dimensional change of 8 per cent rising to 14·5 per cent after 30 minutes. The new heat-resisting types show no dimensional change, or change in other properties even after 30 minutes immersion in boiling water.

Dentures based on Acrylic Resins. The traditional material for making dentures has been hard rubber. For a number of years various plastics materials have been tried for the same purpose. Since rubber became a scarce material this trend has grown stronger. Cellulose nitrate had been tried. Although it was tough, hard, and easily handled it had disadvantages so that it did not give complete satisfaction. Dentures based on phenolic resins have found fairly wide use. The hard, smooth finish and low moisture absorption were favourable features, but they tend to deteriorate with time and are difficult to repair. Polystyrene and vinyl resins have also been employed. Methyl methacrylate resins were introduced about 1936, and latterly they have attained a great measure of success. At the present time methacrylate resins are outstanding for the preparation of dentures. They are also being used for making the actual teeth, although this development is at an early stage of development.

In general, methyl methacrylate is the material used having the best all-round characteristics for the purpose. In this country the Kallodent[12] process was initially developed at an early stage by Imperial Chemical Industries Ltd., and pioneered the evolution of methyl methacrylate as a dental material. The material has been made available to dentists in a number of forms. At first a rod of methyl methacrylate suitably pigmented was extruded into a suitable dental mould. Another technique employed methyl methacrylate powder, which was moulded under temperature and pressure.

The latest technique is to use two materials: (1) methyl methacrylate polymer in the form of powder, and (2) methyl methacrylic monomer. The two are mixed to form a paste which is packed into the dentist's casting, and is then heated under controlled conditions, during which time it sets to a homogeneous polymer. A number of proprietary types of materials are already available in this country.

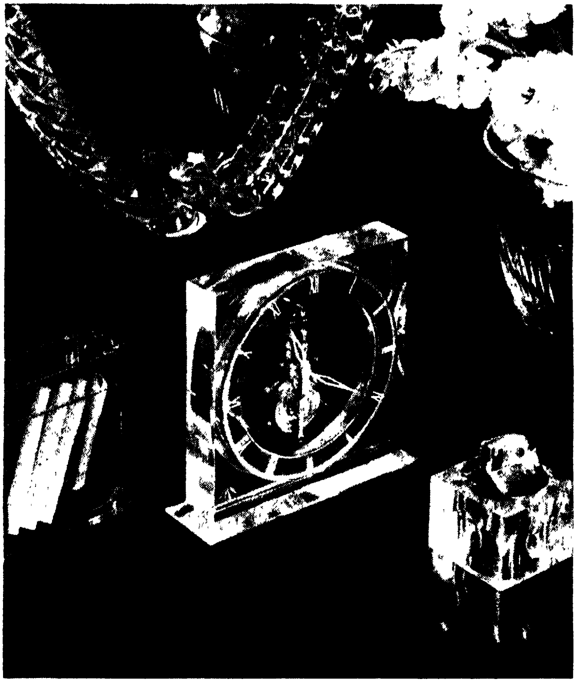


Fig. 220. Typical articles fabricated in methyl methacrylate resin

Clearly one of the most critical features is the moisture absorption. The water absorption of methyl methacrylate, while a little higher than that of hard rubber, does not adversely affect its behaviour in service. No extractable material is obtained from methacrylate mouldings. One of the outstanding advantages of methyl methacrylate dentures is their lightness in weight as compared with hard rubber. They are, in fact, about half the weight in most cases. This has a profound influence on the comfort. The temperature resistance is adequate, quite effective up to 50° C., which is as high as is necessary. Methacrylate resins are somewhat harder than hard rubber dentures.

Methacrylate resin dentures are available in any desired shade in contrast to the limitations of rubber dentures. The colour stability of methacrylate dentures has been found to be quite adequate. This is based on actual usage for many years.

In the past the chief problem in moulding the material was to avoid porosity owing to the use of high temperatures. The latest methods eliminate this by setting methyl methacrylate dentures at a comparatively low temperature, i.e. at about 80° C., for an hour, and then gradually raising the temperature to 100° C., at which about thirty minutes is required.

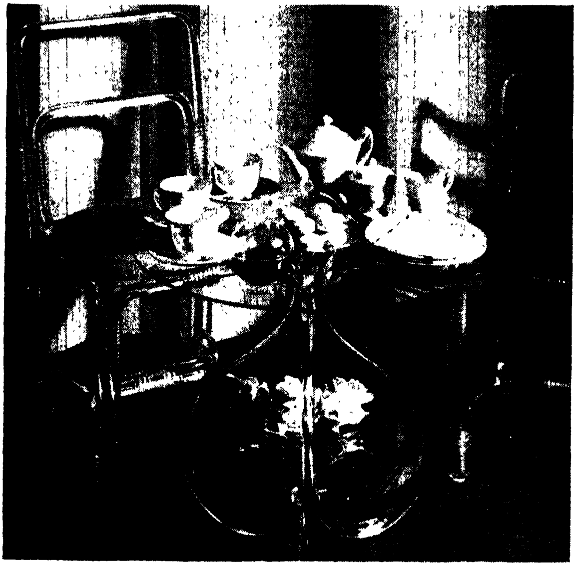


Fig. 221. The use of methyl methacrylate resins for furniture

The general characteristics of methacrylate resins are extremely satisfactory compared with other materials. The material does not present many processing difficulties. Repairs may be carried out quite readily. As a result, it is being more widely used for dentures.

Methyl Methacrylate Polymers for Arts and Crafts. The brilliant clarity of methyl methacrylate accompanied by its attractive chemical properties have led to many unexpected applications. It is very easily worked, and can thus be turned, carved, and handled with some ease. As a consequence the material has been taken up by sculptors, etc., for the production of many *objets d'art.* Most attractive carved articles have been made, such as candlesticks, vases, and so on.

Many decorative articles have been made from methyl methacrylate resin ranging from personal gadgets to a whole host of household accessories. Perhaps of particular interest has been the utilisation of these resins for decorative furniture. This is an interesting trend which may go far.

Other Acrylic Resins. While methyl methacrylate is by far the predominating material in the class of acrylic resins, many others are beginning to acquire industrial significance. In particular they are being used as solutions, although there are some applications of solid compositions. Neher[15] has given a good description of them.

Table 139

Plasticity of Polymerised Acrylic Acid Derivatives*[13]

Polymer	Thickness mm.	Temp. °C.	Time Min.	Elongation at End of Time Interval %	Recovery or "Rebound" %
Co-polymer A (largely ethyl methacrylate, some methyl acrylate) . .	0·08	42	10	100	65
Co-polymer B (some ethyl methacrylate, largely methyl acrylate) . .	0·20	21	10	100	65
Co-polymer B (some ethyl methacrylate, largely methyl acrylate) . .	0·20	33	6	28	137
Methyl acrylate (high) . . .	0·20	21	10	35	130
Methyl acrylate (high) . . .	0·20	33	2	27	138
Methyl acrylate (low) . . .	0·20	30	10	151	14

* Films stretched 165% and recovery or "rebound" noted.

The polymerised acrylic acid esters have been known for years and were early recognised as products of technical importance.[16] As the most important among them the methyl ester, ethyl ester, and butyl ester may be mentioned. Films made of these esters have a low rebound elasticity, but a "handle" similar to that of soft rubber, the relative hardness of the films decreasing in the sequence: methyl ester, ethyl ester, butyl ester.

Klein and Pearce[13] have considered the polymers of methyl and ethyl esters of acrylic and methacrylic acids, and the copolymers of these four esters as coating materials. It is possible to produce these resins with a wide range of physical properties. The characteristics of the film vary from a sticky, rubbery, almost liquid material to a hard, tough, almost brittle product. Thus polymethyl acrylate can be stretched 1,000 per cent. The elasticity of these materials is limited in the sense that recovery is quite slow.

The tensile strength and elongation vary with composition. According to Pearce and Klein, the films commonly used in coatings generally fall in the range between 200–400 kg. per sq. cm.

The field is much wider than these resins. Although any of the methacrylate resins can be used for this purpose, n-propyl, n-butyl, isobutyl, or copolymers of methyl with the softer resins are readily adapted for use as finishes. The extensibility and elasticity of poly-n-propyl and poly-n-butyl methacrylate films, particularly the latter, more closely resemble polyacrylate than polyethyl methacrylate films used by these investigators.

The acrylic ester resins are definitely softer than methacrylic ester resins, but as the alcohol used in the methacrylic ester grows longer, so the resin formed becomes softer, even becoming liquid, for example, in the case of lauryl methacrylate.

According to the technicians of Du Pont de Nemours,[4] "The effect of the structure of the alcohol group is shown by the properties of the butyl methacrylate polymers. The plasticity of the isobutyl and secondary butyl ester polymers is less than that of the normal butyl. The effect of an alcohol containing a carbocyclic or heterocyclic ring is to give a harder, less plastic resin than an aliphatic alcohol of approximately the same molecular weight. This effect is very pronounced in the case of p-cyclohexyl phenyl methacrylate. The influence of four substituents in the beta position of ethyl methacrylate is shown. Chlorine has no effect upon the plasticity. A phenyl and methoxy group increases the softness to the same extent. An ethoxy group gives a soft polymer. With two methacryl groups in one molecule, as in the case of ethylene glycol dimethacrylate, an insoluble and infusible polymer results. The same type of polymer is obtained from methallyl methacrylate.

The softness of the higher aliphatic methacrylate resins can be decreased by interpolymerisation with the harder methyl ester. A resin of any degree of plasticity can be prepared, varying from the hard methyl methacrylate polymer to the viscous liquid polylauryl methacrylate, by copolymerising the appropriate monomers in the correct proportions."

All polymers have many important properties in common: (*a*) clarity, (*b*) light resistance, (*c*) resistance to petroleum hydrocarbons, (*d*) good adhesion to most surfaces, (*e*) good electrical properties, (*f*) good durability. Although they burn, the flammability is no worse than that of cellulose acetate.

TABLE 140
PROPERTIES OF METHACRYLIC ESTERS[4]

Methacrylate	Monomer			Polymer-moulded Disc	
	B.p. °C.	B.p. Mm.	Density at 20° C.	Softening Temp. °C.	Description
Methyl	100·3	760	0·945	125	Clear, hard, strong
Ethyl	116·5–117	760	—	65	Clear, tough
n-Propyl	141–143	756	0·921	38	Clear, tough, flexible
Isopropyl	125	760	0·888	95	Clear, strong
n-Butyl	51–52	11	0·894	33	Clear, flexible, strong
Isobutyl	46–47	13	0·884	70	Clear, slightly brittle
sec-Butyl	53–57	18	0·890	62	Clear, slightly brittle
tert-Amyl	67–68	20	0·887	76	Clear, brittle
Diisopropyl carbinol	72–75	9	0·876	60	Clear, very brittle
Octyl	105	5	—	< Room Temp.	Clear, gel.
Lauryl	142	4	—	< Room Temp.	Clear, viscous liquid
Phenyl	83–84	4	1·053	120	Clear, very brittle
o-Cresyl	98–103	5	1·031	106	Clear, very brittle
Cyclohexyl	71–74	5	0·959	105	Clear, slightly brittle
p-Cyclohexyl phenyl	M.p. 67–68	—	—	145	Hazy, brittle, very hard
Furfuryl	80–82	5	1·055	78	Brown, hard, brittle
Tetrahydrofurfuryl	81–85	4	1·039	60	Transparent, brittle
β-Chloroethyl	61–64	11	1·106	68	Clear, colourless, tough
β-Phenyl ethyl	110–117	5	1·018	40	Clear, slightly brittle
β-Methoxy ethyl	65–67	10	0·990	30	Clear, tough
β-ethoxy ethyl	91–93	35	0·996	< Room Temp.	Clear, rubbery
Ethylene glycol mono-	85–86	5	1·079	70	White, slightly brittle
Ethylene glycol di-	83	2	—	—	Infusible, insoluble, solid
a-Methyl allyl	57–59	15	0·921	—	Infusible, insoluble solid

Acrylic resin films are more extensible than any flexible cellulose lacquers. They are being widely used where stretching and flexing are required, e.g. on rubber and on fabrics. They have good adhesion to most surfaces, the softer films being best. These films have excellent durability. Although they burn, the flammability is no worse than cellulose acetate. Although adhesion is good, it is improved by baking.

TABLE 141

PHYSICAL PROPERTIES OF SOME METHACRYLIC ESTER POLYMERS[26]

Property	Methyl	Ethyl	n-Propyl	n-Butyl	Isobutyl
Density at 25° C.	1·19	1·11	1·06	1·05	1·0
Pfund hardness at 25° C.	220	141	100	1	210
Thermal yield-point, °C.	125	65	38	30	70
Tensile strength, lb. per sq. in.	9,000	5,000	4,000	1,000	3,400
Impact strength (Dynstat kg. cm. per sq. cm.)	10·5	7·1	6·5	11·5	1·6
Refractive Index	1·490	1·485	1·484	1·483	1·477
Extensibility of 5-mil films, per cent at break	4	7	5	230	2
Toughness (area under load-elongation curves)	98	174	76	1,000	23
Dielectric strength of 0·05 in. film, volts per mil	740	—	650	625	—
Power factor at 25°C. and 60 volts per cent	6·5	—	3·8	6·2	—

Corrosion resistance of the harder types are extremely good. They are unaffected by hot and cold water, they withstand alkalis, sulphuric acid, acetic acid and so on. They are unaffected by mineral oils, petrol, greases, and aliphatic hydrocarbons. They are swelled and dissolved by chlorinated hydrocarbons, aromatic hydrocarbons and esters. They withstand ozone and ultra-violet light.

They are soluble in toluene, xylene and other aromatic hydrocarbons; in ethylene dichloride, trichlorethylene, etc. ; esters such as ethyl acetate and butyl acetate; ether alcohols and ether esters. Solutions, are fairly viscous, but such solutions can be sprayed, brushed, dipped or roller coated.

These soft acrylic resins are compatible with nitro-cellulose in all proportions. They are also compatible with plasticisers such as dibutyl phthalate, tricresyl phosphate, chlorinated diphenyl, and so on. Many are soluble in dibutyl phthalate. Apart from rosin, they do not mix with any other resins or gums.

There are already a number of commercial materials based on these products.

Wood[28] has summarised the reasons for the growing use of acrylic resins for coatings and finishes as:

1. Permanence, clarity and transparency. This is particularly important where top finishes are needed in the motor-car industry, also for the final treatment of chromium and stainless steel shop fronts, copper screens, silver trophies and other types of metal work. Incidentally, highly transparent acrylic resin solutions are being used in lampshade manufacture, and for the preservation of drawings and other perishable objects of art.
2. Resistance to water, alcohol, petroleum and coal-tar hydrocarbons. As coatings for paper-cap linings and paper boxes this property of resistance is importance.
3. Resistance to mineral and vegetable oils, greases, ozone, alkalis and dilute acids. Several industries are interested in finishes possessing these properties. The canning trade is, for instance, concerned about the ability of acrylic resins to protect tinplate and prevent corrosion due to fruit acids.
4. High electrical resistance, and recommended as insulating coatings.
5. Resistance to chemical fumes, moisture, etc.
6. Resistance to heat when used as an ingredient of certain baking enamels.
7. Good adhesion and flexibility. In the production of base coatings for textiles, artificial leather finishes, rubber lacquers, etc., the new acrylic resins are being used to a growing extent. Ability to resist continual flexing either at ordinary or low temperatures is particularly important in the case of leather finishes.

According to Pearce,[18] at present they are being used in clear coatings for metals, high temperature baking enamels which are not discoloured at temperatures of 200° C. to 260° C., fume proof coatings, interior truck and tank coatings, and coatings for various textiles. A large percentage of the acrylic resins are being used for defence purposes.

Synthetic Acrylic Latices. Acrylic acid ester polymers are available in the form of synthetic latices. Acrylic acid can be esterified with numerous alcohols to give a very wide variety of monomers, which allows a correspondingly wide scope for the polymer dispersions. The acrylate monomer is emulsified in water together with a suitable emulsifying agent. A small amount of catalyst such as hydrogen peroxide is added. When heated at 70° C. to 90° C. a latex is formed, the nature of which varies according to the time of heating.

The polymerised dispersions dry out to give more or less flexible films having good adhesive properties, and which do not require the addition of plasticisers. These products are not saponifiable and are very resistant to moisture. The behaviour of the individual acrylic acid esters allows them to be put to the most diverse applications, and special requirements can be met by skilful blending. Softness and flexibility, heat resistance and water resistance tend to improve with increasing length of the alcohol portion, while the adhesion and the solubility in benzene also rise in the same direction.

TABLE 142

CHARACTERISTICS OF A TYPICAL CO-POLYMER ACRYLATE FILM

Specific gravity	1·15
Refractive index	1·484
Tensile strength	7,100 lb./sq. in.
% elongation	10
Water absorption (48 hours)	0·85%
Dielectric strength	1,200 volts/mil.
Power factor (1,000 cycles)	3·3
Dielectric constant (1,000 cycles)	2·9

The aqueous emulsions are widely used for leather finishes, being applied by hand to the grain of the leather. Leather coatings demand very high values in respect to flexibility and adhesion. These resins do not detract from the natural feel of the leather.

It is of interest to consider the new methacrylate polymer finishes which are employed as leather finishes and coatings for leather cloth. According to Du Pont de Nemours,[5] the most suitable resin is the polymer of n-butyl methacrylate. Polymers of the higher alcohol esters, namely, propyl, isobutyl, amyl, hexyl, heptyl, and octyl, alcohol esters are also suitable, but the heptyl and octyl methacrylates provide a finish somewhat softer in nature than that of the n-butyl methacrylate polymer. The methacrylate monomer is polymerised and emulsified to form a finish that can be applied with a swab covered with upholstery plush and finished off by spraying. Advantages claimed for emulsified methacrylate finishes may be summed up as follows:

a. High flexibility at ordinary and low temperatures.

b. Small proportions of plasticiser needed, which means that the finish is more stable than can reasonably be expected in the case of nitro-cellulose finishes.

c. The finish may be quickly and easily applied.

d. There is no masking of the grain, and the finished leather has not an artificial or doped appearance.

e. Finish may be employed for priming or top finishing by merely altering the formula.

f. Fire and health hazards greatly reduced as compared with finishes formulated with solvents.

In the textile field aqueous dispersions of acrylic acid ester polymers are used as permanent finishes for stiffening and for increasing the tensile strength and wear resistance of impregnated fabrics. They require no baking, give striking effects when used at low concentrations and are fast to washing. The harder forms of resins give stiffness and sheerness to a fabric, while the softer ones give body and fullness with a mellow handle. Their use materially enhances the strength of textiles, gives brighter, clear colours and long-lasting finishes.

Many of these aqueous dispersions have already become available for waterproofing, fabric finishing and so on. They are especially useful for the production of coated fabrics, as in artificial leathers and oilcloths.

The methacrylic acid ester polymers are somewhat different. They give much harder surfaces and have higher melting points. They also have much lower adhesive properties. Their dispersions are used where tacky films are required, which must dry to a hard surface and must have high heat resistance. They are particularly effective as clear lacquers on metals, where they prevent tarnishing. They are recommended as adhesives for textile treating and finishing materials. One example of their use is as stiffening agents for collars.

German Acrylic Polymers. The I.G. produced large quantities of acrylic polymers which they called Acronals.[30] The peak wartime output of polyacrylate emulsions (25 to 50 per cent solids) was 500 to 600 short tons per month. Highest production of polyacrylate solutions (20 to 50 per cent solids) was 125 tons per month. Peak output of polyacrylate solids was 8 to 10 tons per month. This was in 1942.

Emulsion Polymers. The compositions of I.G. acrylate emulsion polymers are presented in Table 143.

Aqueous polyacrylate dispersions, have low viscosity in spite of their high concentration. They can therefore be applied as thick coatings or impregnations in one operation. Polymethyl and polyethyl acrylate dispersions found extensive use in textile sizings, artificial leather and can lacquers. A stabiliser known as Emulphor O was sometimes added to the extent of 1 to 2 per cent; this compound was made from 20 mols ethylene oxide and 1 mol C_{15}–C_{17} Fischer-Tropsch fatty alcohols.

One of the largest outlets for the acrylic resin emulsions was in shoes. Other important uses were for artificial leather, leather treatment, bookbindings, adhesives, surface coatings and so on.

Leather substitutes were made by impregnating absorbent paper fibres or a cheap felt made of lint, rayon fluff and cotton waste. The

TABLE 143

ACRYLIC POLYMERS PRODUCED

EMULSION POLYMERS

Acronal type	*Composition*	
I D	Polymethyl acrylate 25% conc. 40% conc.	
II D	Polyethyl acrylate 25% conc. 40% conc.	
IV D	Polybutyl acrylate 25% conc. 40% conc.	
200 D, (50%)	Methyl acrylate Vinyl isobutyl ether Acrylonitrile	15 50 35
250 D, (40%)	Methyl acrylate Vinyl benzoate Acrylic acid	80 20 1
300 D, (50%)	Butyl acrylate Vinyl acetate Vinyl chloride	1 1 1
400 D, (40%)	Methyl acrylate Vinyl isobutyl ether Styrene Acrylic acid	66 20 12 2
430 D, (50%)	Methyl acrylate Vinyl isobutyl ether Acrylonitrile	30 50 20
450 D, (40%)	Ethyl acrylate Vinyl isobutyl ether Styrene Acrylic acid	66 20 12 2
500 D, (50%)	Butyl acrylate Vinyl acetate Acrylic acid	49 49 2
550 D, (50%)	Methyl acrylate Vinyl isobutyl ether Acrylic acid	27 27 1
600 D, (40%)	Ethyl acrylate Vinyl isobutyl ether Acrylic acid	76 22 2
Latekoll S, (30%)	Polyacrylic acid	
Latekoll N, (25%)	Sodium polyacrylate	
Latekoll A, (10%)	Ammon. polyacrylate	

Latekolls were sold to the textile and carpet industries as stiffeners and to the lacquer and paper industries as binders. A related product, but one compatible with a greater variety of products than the Latekolls, is Collacral N. This is composed of 75 per cent by weight of acrylonitrile and 25 per cent methyl acrylate. The dispersion is saponified by ammonia:

This material approximates casein closely in properties and is a very good thickening agent.

Solution Polymers. The chief solvents used in the solution polymerisation process were ethyl acetate, benzene and toluene. Polymethyl acrylate solutions were used largely for making lacquers and as an interlayer for a safety glass; it was plasticised with 20 per cent of dibutyl phthalate for this latter purpose. Polyethyl and polybutyl acrylates (50 to 150 parts) were used with cellulose nitrate (100 parts) for aircraft coatings. A special lacquer grade of polyethyl acrylate was made as a 50 per cent solution in ethyl acetate and had a K-value of 50.

Polybutyl acrylate solution polymers were prepared as a 20 per cent solution in ethyl acetate (K-value 60), 50 per cent solution in ethyl acetate (K-value 50), and 30 per cent solution in 70 parts acetone and 30 parts solution in 70 parts acetone and 30 parts benzene (K-value 80).

Acronal 500 solution polymers were made of the same composition as the emulsion polymers. They were produced as 40 per cent solutions in ethyl acetate and benzene, respectively; their K-values were in the range of 55 to 60. Acronal 700 solution polymer was used as a coating on metals.

The Acronal solutions dry to pliable rubberlike films.

Acronals IV and 500 have the best resistance to water. Acronals I, II, and 500 are suitable for the production of artificial leather, oilcloth and coated materials of all kinds. Since they are made without emulsifiers, they are satisfactory for raincoat manufacture. These two materials are also put to very good use as sizing materials in the textile industry and as adhesives.

Solid Polymers. The Acronal resins are easily soluble in esters, ketones, benzene, and chlorinated hydrocarbons. Solubility in alcohols is limited. Acronal I was polymethyl acrylate, Acronal II was polyethyl acrylate and Acronal IV was polybutyl acrylate. Acronals I and II are not soluble in aliphatic hydrocarbons and mineral oils; these chemicals cause Acronal IV to swell. Their chief uses were as compounding ingredients for lacquers, pressure-sensitive adhesive tapes, cable coverings, and as plasticisers for both polyisobutylene rubber and synthetic rubbers.

REFERENCES

1 Bauer. G.P. 571,123/1928; B.P. 313,877/1929.
2 Bauer and Lauth. G.P. 662,157/1932.
3 Crawford. B.P. 405,699/1932.
4 Du Pont de Nemours. *Ind. Eng. Chem.*, 1936, **28**, 1161.
5 Du Pont de Nemours. B.P. 533,343/1940.
6 Fittig. *Ann.* 1877, **188**, 54.
7 Gates and Renfrew. B.P. 505,012/1939.

8 High Refractive Index. B.P. 528,438.
9 HILL. B.P. 395,687/1933.
10 I.G. B.P. 358,534 (Emulsions); G.P. 362,366; B.P. 458,534/1931.
11 KAHLBAUM. *Berichte*, 1880, **13**, 2348.
12 Kallodent. Imperial Chemical Industries (Plastics), Ltd.
13 KLEIN AND PEARCE. *Ind. Eng. Chem.*, 1936, **28**, 637.
14 MOUREU. *Bull Soc. Chim.*, 1893, **9**, 386.
15 NEHER. *Ind. Eng. Chem.*, 1936, **28**, 267.
16 NEHER AND HOLLANDER. U.S.P. 1,937,323/1932.
17 Optical Lenses. B.P. 510,007/1939.
18 PEARCE. *Paint and Varnish Products*, 1942, **22**, 31.
19 REDTENBACHER. *Ann.* 1943, **47**, 113.
20 RENFREW. B.P. 398,189/1933; B.P. 398/855/1933.
21 RENFREW AND CARESS. *Chem. and Ind.*, 1937, **56**, 682.
22 RÖHM. *Berichte*, 1901, 34, 593.
23 RÖHM AND HAAS. B.P. 304,681/1930.
24 RÖHM and BAUER. G.P. 656,421/1939; 693,140/1940.
25 STRAIN. U.S.P. 2,030,901/1936.
26 STRAIN, KINNELLY AND DITMAR. *Ind. Eng. Chem.*, 1939, **31**, 382.
27 WEGER. *Ann.*, 1883, **221**, 79.
28 WOOD. *Plastics*, 1942, **6**, 127.
29 Photographs by courtesy of Imperial Chemical Industries (Plastics), Ltd.
30 C.I.O.S. 363. XXVII-85.
31 C.I.O.S. XXXIII-23, p. 159.

CHAPTER XXV

POLYVINYL ACETATE AND ITS PLASTICS

POLYVINYL acetate is one of the most important plastic materials. In spite of this it is little used as a plastic. On the other hand it is the parent material for many of the leading commercial products. In particular it is used directly to produce polyvinyl alcohol, polyvinyl formal, polyvinyl acetate, polyvinyl butyral, etc.

Vinyl acetate together with vinyl chloride is used in the preparation of the leading commercial copolymers, i.e. the Vinylite materials.

It is evident, therefore, that without adequate sources of polyvinyl acetate, a country is badly handicapped in dealing with these plastics. That is the position in Great Britain up to the present time, and explains why our contributions in this field have been small.

Vinyl acetate was discovered in 1912 by Klatte.[9] It was subsequently found to polymerise without much difficulty.

Vinyl acetate is prepared by passing acetylene into glacial acetic acid containing a mercury salt as catalyst. Mercuric sulphate is a most widely used catalyst. Vinyl acetate is a colourless mobile liquid boiling at 73°C. It can easily be polymerised by heating in the presence of benzoyl peroxide, etc., to give the resinous polyvinyl acetate products which have become commercially important. Vinyl acetate itself polymerises to give solid materials which are notably useful for adhesives. Its most important attribute, however, is the ease with which it copolymerises with other monomers. The use of catalysts was first described by Klatte and Rollett in 1917.[10]

The I.G. plant at Höchst was designed to make 1,000 tons vinyl acetate per month.[22] Pure acetic acid vapour, 15 per cent, and acetylene, 85 per cent, were preheated up to 200°C. and led into a furnace over active carbon impregnated with zinc acetate. It passes into a distillation column as a mixture of acetylene, acetone acetaldehyde, acetic anhydride and vinyl acetate. After cooling, vinyl acetate and acetic acid pass into a second still, where they are separated.

The Germans attached much importance to the polymer for a number of polymers were made by a variety of processes.

Mowolith 20K	Having molecular weight			3,500
30K	,,	,,	,,	8,500
50K	,,	,,	,,	25,000
70K	,,	,,	,,	40,000
90K	,,	,,	,,	60,000

A typical emulsion polymerisation is carried out as follows: The polymerisation vessel is enamelled and jacketed with capacity of 3 cubic metres, and is fitted with a stirrer. In it is placed 1,050 kilos of aqueous solution containing 5 per cent aqueous polvinyl alcohol, 1·05 kilos formic acid and 3·3 kilos 40 per cent hydrogen peroxide. After this 150 kilos vinyl acetate is added and the temperature brought up to 70°C. Over 2 hours a further 900 kilos vinyl acetate is added. Polymerisation proceeds for a further 1½ hours, temperature not being allowed to go beyond 90°C.

Polyvinyl acetate is available as a white or colourless resin which softens at a very low temperature, about 38° C. It has no taste or odour, is non-toxic, and quite thermoplastic. It is available in a number of forms according to the degree of polymerisation. This factor is most clearly evident in the viscosity of its solutions, the viscosity varying almost directly with the degree of polymerisation. The resins have fairly high water absorption. They are soluble in most of the ordinary solvents. They are extremely stable to heat and light, and do not discolour under long exposure to sunlight or ultra-violet light.

They are compatible with many other natural and synthetic resins; in particular they are completely compatible with nitro-cellulose, with a number of alkyd resins, and with phenol formaldehyde resins.

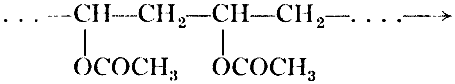
Applications of Polyvinyl Acetate. Polyvinyl acetate is outstanding as an adhesive. It has excellent adhesion to almost every type of surface. In consequence it has found wide commercial application as an adhesive for materials such as cloth, paper, porcelain, metals, leather, wood, glass, etc. Plastic compositions can be made best of polyvinyl acetate, although the low softening point renders them somewhat unattractive. Fillers and plasticising agents can be incorporated. It is difficult to mill owing to the low softening point and the adhesion to rolls, etc.

Applications of 1,000 tons a year in Germany were divided between:

30%	intersoles of shoes
10%	adhesives
15%	laminating purposes
45%	interior matt and glossy paints

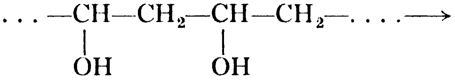
Polyvinyl Alcohol. The monomeric material vinyl alcohol has so far not been isolated. It is, of course, isomeric with ethylene oxide. Nevertheless, the polymer of polyvinyl alcohol is a material of some commercial importance. It is obtained by the hydrolysis of polyvinyl acetate. This was first carried out by Herrmann and Haenkel,[7] who found that they could hydrolise polyvinyl acetate by means of either acid and alkali.

In the United States polyvinyl alcohol is the basis of synthetic elastic material known as Resistoflex. It is made by Du Pont de Nemours.[15] The raw materials are available as white powders which are odourless, tasteless, and soluble in water.



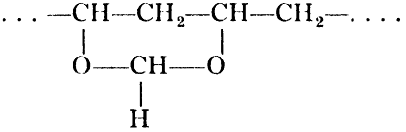
$$\ldots-\underset{\substack{|\\ \mathrm{OCOCH_3}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{OCOCH_3}}}{\mathrm{CH}}-\mathrm{CH_2}-\ldots\longrightarrow$$

Polyvinyl acetate



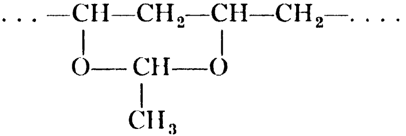
$$\ldots-\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH}}-\mathrm{CH_2}-\ldots\longrightarrow$$

Polyvinyl alcohol



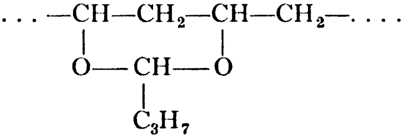
$$\begin{array}{l}\ldots-\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH}-\mathrm{CH_2}-\ldots\\ \quad\ \ |\qquad\qquad\ \ |\\ \quad\ \mathrm{O}-\underset{\substack{|\\ \mathrm{H}}}{\mathrm{CH}}-\mathrm{O}\end{array}$$

Polyvinyl formal



$$\begin{array}{l}\ldots-\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH}-\mathrm{CH_2}-\ldots\\ \quad\ \ |\qquad\qquad\ \ |\\ \quad\ \mathrm{O}-\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{CH}}-\mathrm{O}\end{array}$$

Polyvinyl acetal



$$\begin{array}{l}\ldots-\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH}-\mathrm{CH_2}-\ldots\\ \quad\ \ |\qquad\qquad\ \ |\\ \quad\ \mathrm{O}-\underset{\substack{|\\ \mathrm{C_3H_7}}}{\mathrm{CH}}-\mathrm{O}\end{array}$$

Polyvinyl butyra

Fig. 222

For commercial use they are best made as copolymers with a small proportion of polyvinyl acetate. They can be made resistant to water by treatment with various reagents, such as formaldehyde, chromium compounds, dibasic acids, or copper ammonium compounds. They can be plasticised and then moulded or extruded under moderate conditions of temperature and pressure to give rubber-like articles, or tubes, or coatings. A wide variety of products are now made, including sheets, gloves, gaskets, diaphragms, washers and tubings.

The outstanding feature of polyvinyl alcohol is the ability to withstand oils, fats, and most organic solvents, including chlorinated hydrocarbons, carbon disulphide, alcohols, esters, ethers, ketones, etc.[5] In fact, it is the only flexible material that is completely unaffected by petrol, oils, and most solvents. It is extremely resistant to the action of oxygen and oxone. For example, when subjected to the oxygen bomb test at 300 lb. pressure of oxygen at 70°C. for ten days it was virtually unchanged. It seems to be almost immune to ageing. Polyvinyl alcohol has high tensile strength and withstands vibration and flexing. Tubing made from it has the singular property of transmitting sound with a minimum distortion and there is no sound absorption by the walls of the tube.

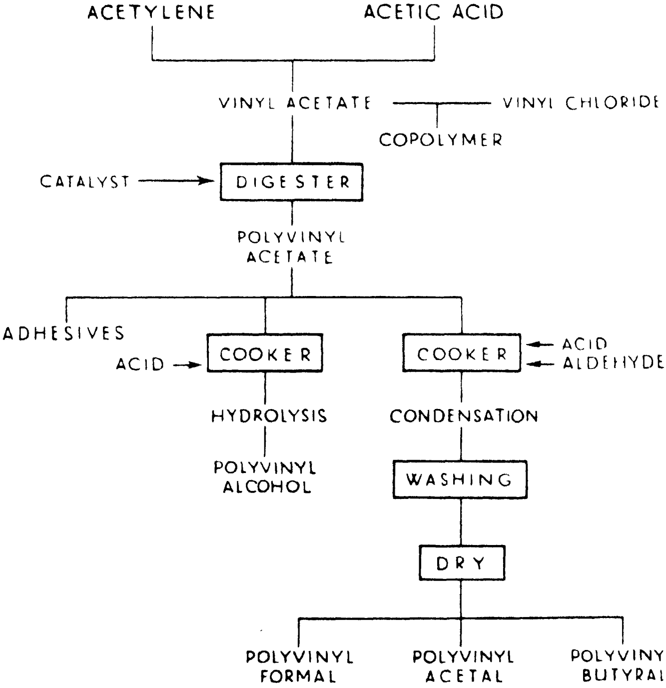


Fig. 223. Flow sheet for polyvinyl acetate plastics

TABLE 144

PHYSICAL PROPERTIES OF RESISTOFLEX

	Extruded	Moulded
Tensile strength, lb./in.^{2}	5,236	2,121
Elongation, %	213	445
Permanent set, %	78	80
Cold flow, %	63·2	63·6
Dielectric strength, volts per mil.	6·1	10·7
Resistivity, ohm/cm.^{3}	$3{\cdot}1 \times 10^7$	$3{\cdot}8 \times 10^7$

Polyvinyl alcohol has even better resistance to abrasion than has rubber. It is only one-twentieth as permeable to gases and liquids.

Photolithographic printing plates are now being made with surfaces based on polyvinyl alcohol. They appear to be admirably suited for the task.

TABLE 145

EFFECT OF SOLVENTS

Tensile strength after 240 hours immersion at room temperature

	lb./sq. in.
Original	5,236
Petrol (with lead)	5,255
Kerosene	5,247
Benzene	5,290
Xylene	5,351
Acetylene	5,340
Trichloroethylene	5,140
Carbon tetrachloride	5,084
Ethyl alcohol	5,779
Ethylene glycol	4,335
Acetone	5,203
Ether	4,980
Butane gas	5,332

Polyvinyl Acetals. Polyvinyl alcohol behaves chemically very much like other alcohols, and can be made to undergo a variety of chemical reactions. An outstanding example is the reaction it undergoes with aldehydes when subjected to heat in the presence of a suitable catalyst. Thus in the presence of sulphuric or hydrochloric acid typical acetals are formed. With formaldehyde polyvinyl formal; with acetaldehyde polyvinyl acetal is formed; and with butyraldehyde polyvinyl butyral is formed. They were evolved by Skirrow and Morrison.[18]

In actual practice the process is carried out direct from polyvinyl acetate, since its hydrolysis, too, may be carried out in the presence of acid. The resin is finally recovered as a white precipitated powder which can be stabilised, purified, and dried.

While the formal, the acetal, the butyral, etc., are white powders showing no elastic properties, other aldehydes such as furfural give products which are distinctly rubbery. However, when suitably plasticised, the white powders develop marked elastic properties. For example, even the toughest material, high molecular weight polyvinyl formal, when milled with an equal amount of tricresyl phosphate gives a transparent rubbery plastic which can be stretched 300 per cent, and will recover its original shape when the stress is released, although somewhat slowly.

The materials obtained in this way have already attained profound commercial significance. To come extent this has been a measure of the elastic properties. The acetal and the formal can be compounded with plasticisers to give flexible rubbery materials, which can be moulded, extruded, calendered, etc.

Properties of Polyvinyl Acetals. The properties of the acetals, or formals, will depend on the extent to which acetaldehyde or formaldehyde respectively have combined, and also the state of polymerisation.

TABLE 146

PHYSICAL PROPERTIES OF POLYVINYL ACETALS

	Formal	Acetal	Butyral
Density at 20° C.	1·23	1·14	1·107
Refractive index at 20° C.	1·50	1·446	1·488
Dielectric strength (volts/mil.)	1,000	1,000	—
Dielectric constant	3·7	2·8	—
Power factor	0·007	—	—
Water absorption (%)	1·3	2·0	4·0
Coefficient of expansion (linear)	·000065	—	—

The polymerisation factor is usually measured by the viscosity of a standard solution, and is directly related to the viscosity of the polyvinyl acetate from which the production commences. These features are best illustrated by the characteristics of some of the best-known materials.

TABLE 147

SOFTENING POINTS OF POLYVINYL ACETALS

	Polyvinyl Acetate	3 centipoise	7 centipoise	15 centipoise
	Degree of Hydrolysis	Softening Points		
Polyvinyl	90%	161° C.	191° C.	220° C.
Formal (Formvar)	90%	170° C.	206° C.	250° C.
Polyvinyl	80%	134° C.	170° C.	188° C.
Acetal (Alvar)	90%	143° C.	180° C.	208° C.
Polyvinyl	80%	114° C.	137° C.	149° C.
Butyral (Butvar)	97%	124° C.	146° C.	163° C.

These figures relate to products of the Shawinigan Company.[4]

Properties of Polyvinyl Formal. The following method[14] describes how polyvinyl formal can be made:

One hundred parts of polyvinyl acetate are dissolved in 185 parts of glacial acetic acid. To this is added 83 parts of formalin and a suitable amount of a mineral acid, e.g. 6·8 parts of concentrated sulphuric acid. This is hydrolised in an enamelled vessel at 70° C. Samples removed from time to time are analysed for the formalin content, which indicate how far the acetate has been converted to formal. When the desired stage has been reached a suitable amount of neutralising agent, e.g. 13 parts concentrated ammonia, is added. The neutralised mass is poured in a thin stream into water. The thread-like material is washed and dried.

Polyvinyl formal can be produced in a number of grades according to the extent to which formaldehyde has combined, and also depending on the degree of polymerisation of the material. They are produced as white granular or thread-like particles having high softening points. These materials are soluble in a limited range of solvents, in chlorinated hydrocarbons, dioxan, acetic acid, and so on. Mixtures of benzene and alcohol are perhaps the best types of solvents. They are insoluble in water, alcohols, benzene, toluene, petroleum fractions, vegetable oils, and so on.

TABLE 148

SOLVENTS FOR POLYVINYL FORMAL

70 parts Benzene plus 30 parts ethyl alcohol
70 parts Toluene plus 30 parts ethyl alcohol
60 parts Xylene plus 40 parts ethyl alcohol
85 parts Monochlorbenzene plus 15 parts ethyl alcohol
70 parts Carbon tetrachloride plus 30 parts ethyl alcohol
80 parts Ethylene dichloride plus 20 parts methyl alcohol

They can readily be compounded and plasticised by the usual mixing technique on heated mixing rolls, or in internal mixers. They are compatible up to about 60 per cent with tricresyl phosphate, dibutyl phthalate, benzyl benzoate, etc. Fillers and colouring materials may be added to give quite attractive materials which may be extruded or moulded. From the moulding point of view they are attractive because there is comparatively little shrinkage.

Up to the present time comparatively few applications have been developed for polyvinyl formal. Two outstanding uses are, however, worth consideration.

Polyvinyl Formal as a Wire-Coating Material. Plastic compositions based on polyvinyl formal are used for insulation for wires and cables, being applied by the conventional extrusion process. However, the material has acquired much wider significance in the related field of thin coatings for wires. Barron[1] has discussed this aspect. Coatings obtained by application from solution are comparable in thickness with conventional enamel coverings. They are superior in a number of important respects, and promise to attain great commercial importance.

TABLE 149

ELECTRICAL PROPERTIES OF FORMVAR 1595

Temperature	Dielectric Constant	Power Factor
29° C.	3·80	·007
61° C.	3·90	·007
91° C.	3·90	·0065

Enamelled wire has physical limitations, notably an inability to withstand abuse in handling. This necessitates the use of protective coverings, such as cotton, paper and silk. These compensate for the defects of the enamel coating. However, they introduce a limitation of great importance, namely, they increase the space occupied by any wire. Insulation of small gauge magnet wire is of the greatest possible importance in view of the fact that every electrical machine contains coils of such wires. This class of wire is insulated with continuous films of baked enamel, or with wrappings of cotton, silk, rayon, asbestos, paper, glass, cellophane, cellulose acetate strip, etc. There are also combinations of these types.

Probably the most important is the baked enamel type, which is often further protected by one of the other forms of covering.

These coatings must have the essential properties of flexibility, extensibility, toughness, temperature stability, and satisfactory dielectric strength.

Since most of the wires are to be used as coils, the insulation must be sufficiently flexible to permit the wire to be wound. It must also be tough enough and possess sufficient abrasion resistance to withstand the treatment in manufacture which is often very rough. The insulation must be able to stand up to the widest possible range of temperature, flexible at very low temperatures and stable at very high temperature.

This latter consideration is one which has presented very promising opportunities for substitution. Insulation must not be affected by high humidity at high temperature. It is also very desirable that insulation should withstand solvents, since many coils and machines are impregnated with insulating varnishes and baked. There are many other corrosive conditions which may be encountered in service, depending on the application, including conditions of exposure to acids and alkalis, salt water, refrigerating liquids, etc.

Superimposed upon all desirable features is the importance of the space factor. This is almost the most important attribute of the insulation—the ability to function efficiently in the thinnest possible coating. Even minute thicknesses of coating when multiplied by the thousands of turns that may be on a coil, assume great significance in machine design and efficiency.

Obviously this is a field offering the greatest possible scope for substitution. The alternatives are to wrap thin films around the wire, to extrude suitable materials in fine coatings on to the wires, or to substitute new materials for application by orthodox enamelling methods. While the first two methods become impracticable with very fine wires, the third method is comprehensive.

Some of the most spectacular examples have been in the field of coatings applied from solutions. In this field of insulation two types of materials stand out. They are the use of polyvinyl formal and the use of nylon.

The success of materials in this type of application depends upon a combination of extremely good physical characteristics, notably abrasion resistance and flexibility together with satisfactory electrical characteristics. In both cases these conditions are satisfied. Successive coatings of the solution of synthetic resin are applied to the wire until the requisite thickness is built up. It is then baked at a high temperature, when the outstanding characteristics appear to be developed, the water resistance in particular being enhanced, the coatings becoming set and no longer thermoplastic.

Coatings based on polyvinyl formal have the outstanding characteristic of being able to withstand mechanical abuse far better than any conventional enamel coating. Polyvinyl formal is applied in the form of solutions as a substitute for enamel. From dilute solutions it is applied to the wire by methods which resemble in many respects conventional enamelling procedure. The requisite number of coatings are applied to give the desired thickness of insulation and this is subsequently baked in order to improve the water resistance and to render it non-thermoplastic. This type of magnet wire has great prospects and is already widely used. Patnode, Flynn and Weh[13] have described the outstanding characteristics of one such type of covered wire.

Applied to wire the coating is strong, tough, and flexible. It retains the excellent electrical and chemical characteristics of polyvinyl formal; it withstands the effects of solvents which may be used on equipment containing the coated wires. Plastic coated wire is several times better than enamel-coated wire as regards abrasion resistance. It is far more extensible. It is able to withstand continued heating for longer periods than ordinary enamel without becoming brittle and cracking.

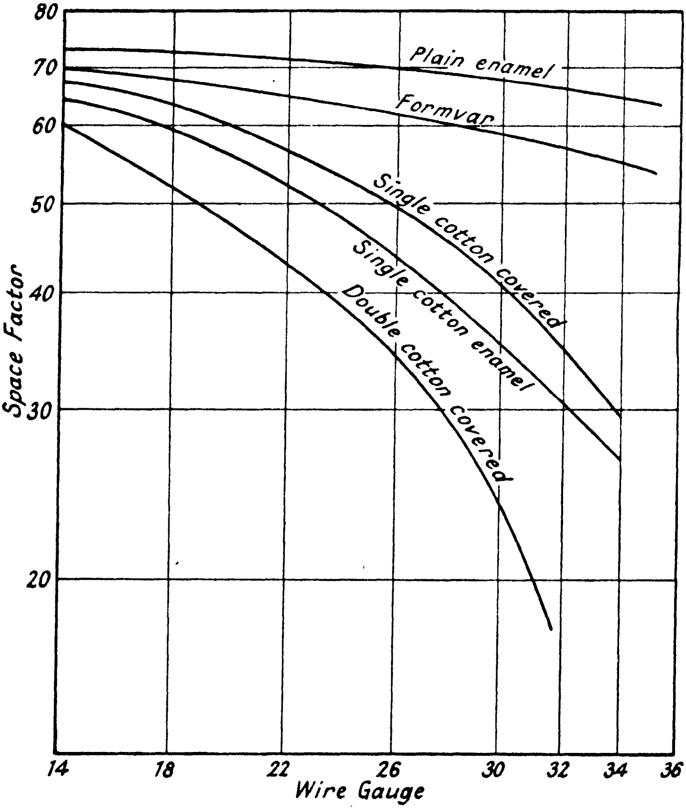


Fig. 224. Space factor curves comparing formvar covered wire with conventional coatings

The Use of Polyvinyl Formal for Laminating Purposes. Polyvinyl formal has been used for the preparation of laminated articles. In particular it is used for making compressed laminated wood employed for propellers. The leading product of this type is known as *Hydulignum*,[8] which is an assembly of packs of conventionally plastic bonded plywood, in turn bonded together with polyvinyl formal. The product is subjected not only to vertical pressure in the normal way, but also to edge pressure at right angles, as a consequence of which the assembly takes on a crinkled section. This appears to offer a number of advantages which are in great part due to the influence of the polyvinyl formal.

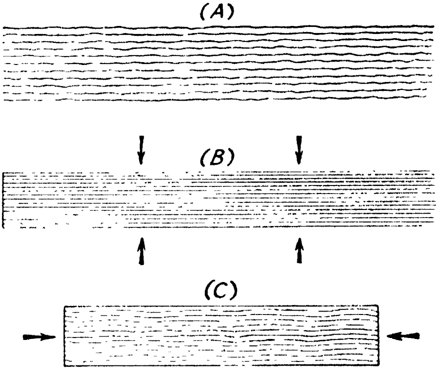


Fig. 225. High density hydulignum

(*a*) Loose pack of coated veneers, (*b*) after first pressure to 60 lb. cu. foot, (*c*) after second pressure to 82 lb. cu. foot

Method of Production of Hydulignum. Birch veneers, each originally $\frac{1}{36}$in. in thickness, are coated with polyvinyl formal solution, formed into packs (about 60 to a pack) and then consolidated under heat and pressure. The density of the material produced in this first operation is controlled to 60 lb. per cubic foot. It has been found that any pressure beyond this point results in spreading of the veneers and consequent loss of strength and density control.

By a second operation, the material is retained under heat and pressure on the top and bottom surfaces, while side pressure is introduced to increase the density by the required amount, which can be as high as 80 lb. per cubic foot. This two-way compression produces a more homogeneous material, and it is preferable to use a thermoplastic resin which enables the material to be made in two operations giving a closer control of density than is possible with any other material. This is a most important characteristic of the material, reflecting on the ultimate balance of the blade.

The material is particularly stable and blocks can be left for an almost indefinite period without deterioration. It is also easier to machine than other high-density materials.

The two-way compression has the added advantage that if any reaction should take place due to shrinkage or expansion under extreme conditions, this is equal in both directions and, therefore, does not result in ovality of blade root.

Another important feature is that veneers of inferior quality can be used entirely without detrimental results.

The following figures show the mechanical properties of Hydulignum:

TABLE 150

Specific gravity	1·31 (82 lb. per cubic ft.)
Tensile strength	45,700 lb. per sq. in.
Compressive strength	21,000 lb. per sq. in.
Shear L.T.	4,540
Shear L.N.	4,480
Modulus of elasticity	4×10^6 lb. per sq. in.

Polyvinyl Acetals. In appearance the polyvinyl acetals are similar to polyvinyl formal, i.e. they are white granular powders. They differ in having lower softening points and in being soluble in a much wider range of solvents. They are soluble in alcohol, benzene, toluene, acetone, chlorinated hydrocarbons, and so on. They are insoluble in petroleum, hydrocarbons, in oils, etc.

Fillers, plasticisers and pigments may be added, as in the case of the formals. So far the application of these materials has been somewhat limited.

Polyvinyl Butyral. The polyvinyl butyrals are undoubtedly the most important materials in this range. This material was specially developed with the object of providing the ideal interlayer for laminated safety glass. Latterly it has acquired an entirely new significance as a very effective substitute for rubber in waterproofing fabrics.

It came about as the result of a long, comprehensive, and expensive joint research scheme undertaken by a number of interested United States concerns. It is already employed for most of the safety glass manufactured in the United States. For this particular application it contains a little polyvinyl acetate and polyvinyl alcohol. It is prepared rather along the lines already described for polyvinyl formal. One method is as follows:[17]

100 parts polyvinyl acetate is dissolved in 93 parts ethyl alcohol, and 93 parts ethyl acetate. To this is added a mixture of 54 parts butyraldehyde, 48 parts water, and 7 parts sulphuric acid. The mix is agitated for 24 hours at 60°C. The acid is neutralised with sodium carbonate, and an almost colourless resin is precipitated by the addition of water.

Polyvinyl butyral is obtained as white flakes having no colour, taste or odour. Its specific gravity is 1·15. It begins to soften at the comparatively low temperature of 65°C., melting at 160°C.

Properties of Polyvinyl Butyral. Polyvinyl butyral is soluble in alcohol, in propyl and butyl alcohols; it goes up in esters such as ethyl lactate; it is also soluble in chloroform, ethylene dichloride, in dioxan, and in the *cellosolve* solvents. It dissolves only partly in acetone. Benzene and toluene swell polyvinyl butyral. It does not dissolve in water, glycerine and glycols, nor is it soluble in carbon tetrachloride. It does not dissolve in aliphatic hydrocarbons. It absorbs up to 4 per cent water on prolonged immersion. It is quite stable towards dilute alkalis, but is decomposed by acids, although it dissolves in glacial acetic acid. It is insoluble in hydrocarbons, oils, and so on.

It may be plasticised by addition of the usual types of materials, e.g. tricresyl phosphate, dibutyl phosphate, dibutyl sebacate, etc. In this manner pronounced elastic properties are developed. Thus the elongation may reach 400 per cent. The yield under pressure is very easy, and the recovery is slow but nevertheless effective. The softening temperature of the plastic is between 60° C. and 70° C. The tensile strength attainable is also quite high, being 2,500 lb. per sq. inch when elongation is 400 per cent, and 8,000 lb. when elongation is only 20 per cent. The flexibility is retained at low temperatures. It ages well, is unaffected by sunlight, and takes up little moisture, depending to some extent on the plasticiser. The refractive index, obviously of great importance for application in safety glass, is 1·488, while the light transmission is about 90 per cent. The material is fabricated by extrusion or by compression moulding. It may be blown, swaged and so on.

A great deal of work has latterly taken place on the principle of introducing reagents such as urea, and thermosetting resins into solutions of polyvinyl acetals with a view to making rubber-like materials which will set on heating.

An interesting development in this field is the application of the vinyl acetal as a substitute for rubber in preparing waterproof fabrics. Haas[6] has been able to transform the thermoplastic material into a thermosetting one. The material is applied to fabric by conventional methods used for rubber, by spreading or by calendering. The manipulation and processing of the material is said to present no difficulties. Curing is carried out under the same conditions as apply for rubber.

Waterproofing Materials. Latterly progress has been made in the preparation of rubber-like materials from polyvinyl formal and polyvinyl butyral particularly, which are finding increasing application in fields hitherto largely monopolised by rubber. A group of proprietary materials along these lines has been brought out by the Monsanto Chemical Company under the name of *Saflex*.[16] There is one outstanding feature, namely, that these materials contain ingredients which enable them to set on heating. In effect there is almost a vulcanising or curing action. One such composition is specially designed for coating of fabrics.

Made up as solutions or doughs, these polyvinyl acetals can be applied to fabric either by spreading, or they may be handled in the solid form by means of the calender. They are finding extensive use for American war equipment. The actual compositions comprise the plastic base, i.e. polyvinyl formal or polyvinyl butyral, suitably compounded with plasticisers, pigments, and the curing agent.

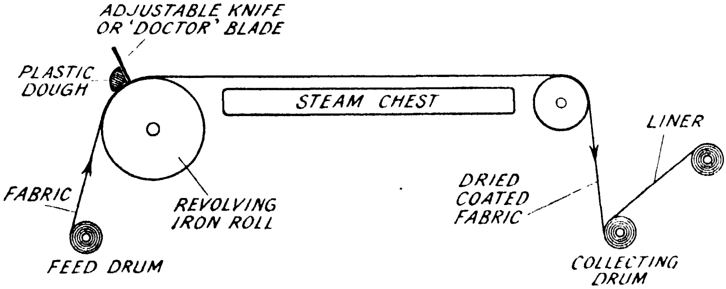


Fig. 226. Diagram of Spreading Process

Solutions or doughs are made up generally in mixtures of alcohol and solvent naphtha. Very wide usage is being made of fabric which has had two coats spread giving a weight of about 1 oz. of coating per sq. yard. The solution employed here contains about 45 per cent non-volatile ingredients.

The solid materials can be applied by means of the calender. In this case they are first made plastic on heated mixing rolls at a temperature of about 180°C., and then fed to the calender. The calender temperatures suggested for its use are top roll 115°C., centre roll and bottom roll 105°C. Very thin films indeed can be applied to fabric by means of the calender. For example, films of 0·002 inches thick present no difficulties. In fabricating such proofed materials cementing must be carried out on the uncured materials. Surfaces may be readily heat sealed. The cements employed are usually solutions in butyl alcohol or alcohol.

The curing conditions involved are summarised as follows:

At 340° F.	5 minutes is required for cure.
At 300° F.	15 minutes is required for cure.
At 265° F.	45 minutes is required for cure.
At 230° F.	90 minutes is required for cure.
At 220° F.	180 minutes is required for cure (approx.).

In practice a cure of 1 hour at 260°F. is recommended.

When these proofed fabrics have been cured the plastic coating acquires greater resistance to solvent, is no longer self-adhesive, and is made resistant to heat. Typical articles which are being made from such materials include raincoats, water-bags, hospital sheetings, and so on. It is also successfully used for making hose, for radiators, etc. Other products include gaskets and packings of many types.

Typical properties of the cured Saflex film are shown in the Table.

TABLE 151

PROPERTIES OF CURED SAFLEX

Specific gravity at 25° C.	1·16
Tensile strength	1,450 lb. per sq. in.
Elongation at break	360%
Low temperature flexibility (0·020 in. film) does not crack when creased at	−50° F.
Water absorption after 48 hours at 25° C.	3·3%
No loss of flexibility.	
It does not affect metals.	
It is very slow burning.	
Resistant to water, dilute alkalis, strong sulphuric acid, aliphatic hydrocarbons.	
Affected by alcohol, aromatic solvents, phenols, etc.	

Laminated Safety Glass. Polyvinyl butyral is now the predominating material for use in laminated safety glass. This is, therefore, a suitable point at which to consider this very important activity.

Laminated safety glass is produced on a very large scale in most industrial countries, especially where there is any significant motor industry. It has played a profound part towards added safety in modern transport. The idea of laminated safety glass as now known was first put forward by Wood[21] in 1905. He proposed to cement a sheet of transparent celluloid between two sheets of glass using Canada balsam. Although this raised some interest, the time was not ripe for its commercial development and it did not get very far.

The first commercial product was developed by Benedictus[2] in 1910. His product "*Triplex*"[19] was based on the same general principles as that of Wood, except that he proposed to use gelatine instead of Canada Balsam as the adhesive. Large scale manufacture of Triplex safety glass was greatly helped by the Great War owing to the demands for the manufacture of gas-mask lenses, goggles, cars, and aircraft.

For some time after the war, production languished largely owing to the fact that the products were technically inferior. Cox introduced the use of cellulose acetate sheet as interlayer in 1923. It was necessary to improve the adhesives, and put in a great deal of work generally, both on glass and with plastic, to carry its use forward. With the rapid expansion of the motor-car industry a considerable amount of work has been devoted to safety glass, and a great measure of success has been achieved.

Laminated glass consists of sheets of glass with an interlayer of plastic material. For ordinary purposes the make-up is generally two sheets of glass with one sheet of plastic. This is a type familiar in motor cars. For special purposes such as bullet-proof glass the number of alternating layers may be considerably greater.

Requirements for Safety Glass. The great difficulties have been effectively to bond the laminations together, and still give the desired visibility. In general the laminated product acquires the properties of other laminated materials, namely an increase in strength, and greater resistance to impact and penetration. It has taken a great deal of effort to evolve the most satisfactory type of glass for the sandwich; that has been a problem of glass technology which was solved some time ago. On the other hand the search for the ideal plastic interlayer has only been solved in recent years. Celluloid held the field until about 1934 when it was ousted by cellulose acetate. Both in turn have been displaced by polyvinyl butyral.

So far as the ideal safety glass is concerned, there are, of course, two lines of approach. One is the development of an organic plastic material which will replace glass altogether, and the other is the development of the perfect laminated safety glass. Up to the present time, in spite of developments with acrylic plastics, no organic material has been found to withstand the severe conditions that are ordinarily satisfactorily taken by glass. For example, glass surfaces on car windscreens have to stand up to the abrasive action of windscreen wipers, which remove not only rain, snow, oil, and the like, but also abrasive materials such as dust, dirt and sand over periods of many years. The evolution of the perfect materials is likely to take some time. In a sense, safety glass is a plastic material whose surface is protected against the severe conditions by sheets of glass.

The conditions of the ideal plastic material used in laminated safety glass may be outlined as follows:

(*a*) It should be as transparent as glass itself.
(*b*) It should be as stable to ageing as glass.
(*c*) It should not be affected by light or heat.
(*d*) It should retain its flexibility at the lowest temperatures likely to be encountered in cold climates.
(*e*) It should have a yield point which will enable it to give in the event of impact.

Use of Cellulose Plastics. Nitro-cellulose as the plastic layer in the composite sandwich has a number of disadvantages. It is not particularly stable towards light and heats. In particular the prolonged exposure to sunlight has the effect of causing decomposition, the decomposition products tending to be brown, and this in due course likewise causes delamination.

Cellulose acetate was an improvement in these respects, although it, too, is actually decomposed by prolonged exposure to sunlight. However, in this instance the decomposition products are colourless and consequently do not interfere with vision. On the other hand, the outstanding disadvantage of cellulose acetate film is the fact that it becomes brittle at a comparatively high temperature, below which it will shatter on impact, and consequently offers no advantage over glass itself. Watkins[20] considered existing types in 1932.

The Problem of Adhesion. One of the very important problems in the preparation of safety glass is the question of adhesion. The types of adhesive agents have been classified (*a*) as materials which do not resemble glass or the plastic used, and (*b*) materials which are related to the plastic.

The first category include materials such as gelatine, glue, isinglass, etc., and various synthetic resins. They are applied by spraying or rolling one surface of each plate of glass with a thin film which is then dried to a suitable texture. The assembly is then put together and bonded by heat and pressure.

The second group contains a variety of cellulose solutions or dopes containing compatible resins to increase the adhesion. Films are applied to the glass and when dry the assembly is bonded by heat and pressure.

The Manufacture of Safety Glass. Several working conditions are fundamentally important:

(*a*) The glass must be perfectly clean.
(*b*) Assembling must be carried out in an atmosphere free from dust.
(*c*) Conditions of humidity and temperature must be maintained.

The following is a typical method employed for a nitro-cellulose layer. The glass plates are cut to size and carefully cleaned. One surface is coated with a solution of a water soluble adhesive. This is dried for some hours. A second layer of adhesive consisting of a nitro-cellulose solution is applied and thoroughly dried. The plates are immersed in alcohol and assembled with the celluloid sheet. The sandwich is suitably protected and pressed between platens of a hydraulic press under heat and pressure.

The technique of applying heat and pressure varies according to the company making the product. The leading procedures are:

(*a*) Standard hydraulic presses heated by steam in which the laminated assemblies are padded for protection.
(*b*) Presses which have flexible diaphragms.
(*c*) Autoclaves where direct hydraulic pressure is applied on the sandwich by means of fluid or alternatively where the sandwich is contained in a rubber bag.

Pressures used are of the order of 200 lb. per sq. inch at temperatures up to 150° C. for times between 5 and 10 minutes.

The question of exposed edges of plastic in laminated glass has in the past been a thorny one. Cellulose products tend to take up a certain amount of water, so that in locations where humid climatic conditions are inevitable, there is a tendency for delamination at the edges. In the normal way it is necessary to take precautions in this respect. So far as the celluloid was concerned the general practice was to have the sheet slightly smaller than the glass plates and fill in the groove thus formed with a bituminous composition.

Safety Glass at Low Temperature. The behaviour of safety glass at low temperature is one of the critical characteristics. The resistance to impact shown by plate glass is not greatly affected by low temperature. Resistance to impact of plastic laminated glass decreases with temperature. The plastic layer progressively has less influence as the temperature is reduced. Both cellulose nitrate and cellulose acetate interlayers showed up badly in this respect. The plastics themselves do not retain plastic characteristics at low temperature. This is the outstanding disadvantage which has led to an intensive search for more suitable safety glass interlayers.

The normal way of testing and comparing laminated safety glass is by noting how they stand up to the impact of a heavy steel ball dropped from varying heights. Almost invariably the glass breaks under impact, but the plastic material holds the broken glass and itself withstands the blows until quite good heights are reached. One method is to note the height from which a 2 lb. steel ball must be dropped to rupture the safety glass.

Polyvinyl Butyral as Interlayer. The search for the ideal sandwich material for safety glass has been very intensive. In the United States a joint research scheme in which all interested firms took part, involving expenditure of about 1½ million pounds, finally solved the problem. This work resulted in the evolution of polyvinyl butyral as interlayer for safety glass.

TABLE 152

INFLUENCE OF TEMPERATURE ON RESISTANCE TO IMPACT OF GLASSES[20]

0·25-INCH PLATE GLASS

Temperature of Impacted Samples		Critical Distance	
°F.	(°C.)	Inches	(cm.)
—70	21·1	6	(15·2)
—32	(0)	7	(17·8)
—13	(—25)	7	(17·8)
—55	(—48·3)	8	(20·3)

CELLULOSE NITRATE–PLATE GLASS LAMINATIONS

Temperature of Impacted Samples		Critical Distance	
°F.	(°C.)	Inches	(cm.)
—70	(21·1)	48	(121·9)
—32	(0)	26	(66·0)
0	(—17·8)	21	(53·3)
—13	(—25)	18	(45·7)
—55	(—48·3)	13	(33·0)

CELLULOSE ACETATE–PLATE GLASS LAMINATIONS

Temperature of Impacted Samples		Critical Distance	
°F.	(°C.)	Inches	(cm.)
—70	(21·1)	48	(121·9)
0	(—17·8)	21	(53·3)
—13	(—25)	18	(45·7)
—55	(—48·3)	13	(33·0)

Thickness of Plastic		Distance required to Break
1 / 1,000 inch	mm.	feet
20	0·508	4·5
25	0·635	6·0
30	0·762	8·5
35	0·889	11·0

The performance of safety glass has been greatly improved by the adoption of the new synthetic resins, the polyvinyl acetals, with polyvinyl butyral as the leading material as the basis of the interlayer film. The material involves the use of plasticisers, and much work has been carried out to find really suitable plasticisers.

At ordinary temperatures the impact resistance of the new types are generally twice as high as that of comparable cellulose acetate types. Much more important is the fact that at zero they are six times as strong.

Partial acetals, in which 2·5 to 7 molecules of polyvinyl alcohol are in combination with each molecule of aldehyde are reported to be exceptionally flexible at low temperatures. This property, in association with the excellent adhesion to glass, and the resistance to moisture, makes them particularly interesting as interlayers.

There is a wide choice of aldehydes in the manufacture of these acetals, but there seems little doubt that butyraldehyde results in the best all-round performance. For any given aldehyde it is found that the adhesion of acetal to glass surfaces appears to decline with increasing aldehyde content, while the flexibility increases. It is necessary, in practice, to effect a compromise, and this is done by using an acetal resin with a ratio of 2·5 to 4 molecules of polyvinyl alcohol to each molecule of aldehyde. Alternatively, the glass surfaces may be treated with a priming coat containing a strongly adherent acetal, such as one with a polyvinyl alcohol; aldehyde ratio of 6·1. The actual interlayer of flexible acetal may have a ratio of 3·5 molecules polyvinyl alcohol to one molecule of butyraldehyde, and may be furthermore plasticised with 40 per cent of diethyl phthalate. This latter composition is prepared as a transparent sheet of about 0·05 inch thickness.

Influence of Plasticisers. Suitable plasticisers play an important part in the make up of these types of laminated glass. Criteria involved in the selection of plasticisers for this purpose include stability to ultra-violet light in order to avoid discoloration of the originally colourless acetal film, and the ability to impart a rubber-like consistency and nerve to the interlayer film. Recent examples include the following: Diethylene glycol tetrahydrofuroate; amyl succinate; diisoamy; maleate; dihexyl maleate; dioctyl maleate; ethoxy ethyl maleatel methoxy ethyl maleate; diethylene glycol succinate ethyl ether; diethylene glycol benzoate butyl ether; diglyceryl tetrapropionate; dibuty sebacate.

There is a tendency for the introduction of newer plasticisers. The Monsanto Chemical Company[12] claimed to obtain exceptional flexibility by using an interlayer of (partially hydrolysed polyvinyl acetate condensed with butyraldehyde) plasticised with about 50 per cent of an easter of diglycollic or thiodiglycollic acid, e.g. digutyl diglycollate. A safety glass on this basis successfully withstood the impact of a two-pound ball dropped from a height of 15 feet at a temperature of −23° C.

One of the plasticisers recommended by Carbide and Carbon Chemicals Corporation[3] is tetraethylene glycol monomethyl ether. The Libby-Owens-Ford Glass Company,[11] concluded aliphatic esters of diglycerol, such as glycerol tetra-acetate were best for the purpose. When tested with the two-pound ball the laminated system stood up to the impact from a height of 21 feet at −18° C.

An outstanding advantage of the butyral type of plasticised interlayer is that the final system does not need to be edge-sealed as a protection against the weather (as is the case with nitro-cellulose and cellulose acetate interlayers). This opens the way to a considerable increase in rate of output of safety glass.

One interesting application where this, it has been suggested, may be important is for use in substratosphere aircraft. Here the projecting plastic edges can be secured to the walls of the structure by such methods as bolting, screwing, or nailing.

Safety Glass at very Low Temperature. Even polyvinyl butyral does not retain flexibility at the very low temperatures involved in sub-stratosphere work, aircraft operations generally, and in severe Arctic conditions. In fact, ethyl cellulose sheeting suitably plasticised is the only plastic to give really adequate performance in these conditions. As a consequence, ethyl cellulose is already being used to some extent in such conditions.

Cutting Laminated Safety Glass. Safety glass can be cut without any difficulty. The top and bottom glass sheets are scratched with the diamond and then cracked. The lower crack is warmed slightly so that the plastic softens. It is then pulled away slightly and the plastic sheet cut.

Polyvinyl Ethers. The polyvinyl ethers are still in a comparatively early stage of development. They have been produced on a fairly large scale in Germany, being the chief application of the Reppe acetylene reaction. The main product is polyvinyl isobutyl ether sold as Igevin I.[23] The vinyl ethers are extremely reactive chemically and offer interesting possibilities both in chemical syntheses and in polymerisation to adhesives and plastic compositions. They can easily be polymerised in either the liquid or vapour phase, with a variety of catalysts. The polyvinyl ethers range from liquids to rubbery solids and waxlike balsams. As adhesives, they have been used in surgical tapes and elastic bandage tapes, where they have been found to be more stable to light and show better storage stability than rubber. They have also been used in pressure-sensitive adhesives for sealing envelopes and paper cartons, in laminating glass, in upholstering, in sealing cellophane and metal foils, and in bonding rubber and other materials to glass.

Copolymers of the vinyl ethers have been prepared with vinyl acetate, acrylic esters, acrylonitrile, styrene, and many other compounds. They have been used as plasticisers and tackifiers for synthetic rubbers and nitro-cellulose. and as modifiers for alkyd and polystyrene resins. In synthetic polishing waxes, resin coatings, and lacquers, the vinyl ether polymers impart a lustrous finish to films which may be normally dull in appearance.

One of the chief uses of Igevin I was as binder for magnetic iron oxide cast on to Luvithem P.V.C. tape for sound recording magnetophone tape. The ethers were also copolymerised with acrylic resins.

REFERENCES

1 Barron. *Journal of General Electric Co., Ltd.*, 1942, **11**, 70.
2 Benedictus. *Ind. Eng. Chem.*, 1933, **25**, 1192.
3 Carbide and Carbon Corp. B.P. 460,230/1937.
4 Formvar. Shawinigan Corp. Technical Data.
5 Gibello. *Rev. Gen. Caoutchouc*, 1941, **18**, 198.
6 Haas. *India Rubber World*, 1942, **106**, 599.
7 Herrmann and Haenkel. Ber., 1927, **60**, 1658.
8 Hydulignum. Technical Data of Hordern-Richmond Co., Ltd.
9 Klatte. G.P. 281,687/1912.
10 Klatte and Rollett. U.S.P. 1,241,738/1917.
11 Libby-Owens Ford Glass Co. U.S.P. 2,205,020/1937.
12 Monsanto Chemical Co. U.S.P. 2,205,420/1937.
13 Patnode, Flynn and Weh. *Ind. Eng. Chem.*, 1939, **31**, 1063.
14 Polyvinyl Acetal Production. B.T.H. Ltd., B.P. 518,006/1936.
15 Resistoflex. Product of Du Pont de Nemours.
16 Saflex. Monsanto Chemical Co. Technical Literature.
17 Shawinigan Chemical Co. B.P. 466,598.
18 Skirrow and Morrison. U.S.P. 1,971,951/1934.
19 "Triplex." Product of Triplex Safety Glass Co., Ltd.
20 Watkins. *Ind. Eng. Chem.*, 1932, **24**, 1187.
21 Wood. B.P. 9972/1905.
22 C.I.O.S. XXVI-11.
23 B.I.O.S. 226.

PART V

OTHER LEADING PLASTICS

CHAPTER XXVI

POLYAMIDE PLASTICS

At the present time consideration of polyamides hinges around the particular group known as *nylon*. In 1943 product was 20 million pounds To-day production must be approaching 100 million pounds per annum.

Nylon is one of the best known and least understood of the plastic materials at the present time. It is of outstanding industrial importance. The term is a generic one, intended to cover polyamides generally. One definition states, "Nylon is the generic name for all synthetic fibre-forming materials having a protein-like chemical structure, derivable from coal, air and water or other substances characterised by extreme toughness and strength." From the chemical angle they are the synthetic resins formed by condensation between aliphatic dicarboxylic acids and aliphatic diamines.

It seems likely that for some time to come its primary impact will be on the textile industry. Yet nylon has very great possibilities as a straightforward plastic which can be manipulated by the usual processes employed in the industry. With the advent of peace there has been a great impetus towards the large-scale moulding of polyamide resins. It has by far the highest softening point of any of the organic thermoplastics.

The technique of production of fibres, bristles, filaments, etc., is very much a plastic process. Although the history of polyamides up to the present time has been largely associated with the Du Pont concern in the United States, yet they have been available here for some time. Nylon is produced in this country at the present time by Imperial Chemical Industries, Ltd., and British Nylon Spinners, Ltd.

The development of nylon is an outstanding example of the benefits accruing from fundamental research. Bolton[4] has described how nylon came into existence. It was clear that the growth of the rayon industry was an indication that "a new fibre could be successfully commercialised if it had outstanding characteristics different from those previously commercially available." In 1928 Carothers began the work on polycondensation leading to the production of many new linear polymers, and in particular to the nylon group. According to Bolton the research leading up to the production of nylon yarn was in three sections:

(*a*) Fundamental research activities providing the basis for the development.
(*b*) The concentration of attention on polyamides leading to the synthesis of a polymer having the requisite characteristics for use as a new fibre.
(*c*) The development of practical processes for the manufacture of chemical intermediates and the polymer, and also the technique for the spinning of the fibres.

The Work on Linear Polymers. Carothers[7] carried out a great deal of the fundamental work on polymers, work now regarded as classic. This work forms the basis of much of the present-day knowledge and ideas on polymerisation.

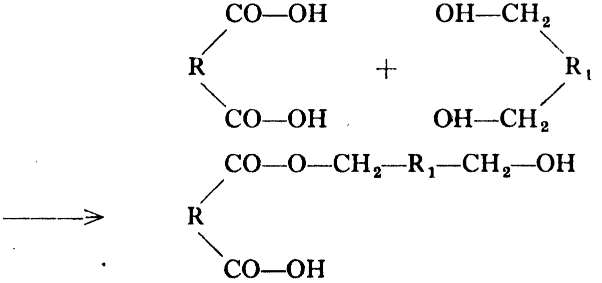
Carothers started by condensing dibasic acids with glycols, the products of which indicated that he was developing long-chain polymers.

Carothers' earlier work established the principles of polycondensation which have provided much guidance in the general study of long polymers. His views may be illustrated by considering the mechanism of polycondensation.

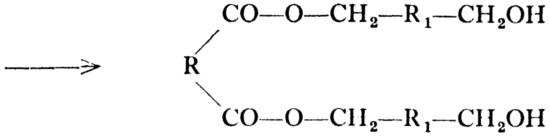
This is the union of a large number of molecules of the same substance or of different substances, reacting between themselves with the elimination during the reaction of water, hydrochloric acid, sodium chloride, etc. Polycondensation can only lead to the formation of large molecules if the product of the initial reaction retains reactive points which can give rise to new condensations. Thus a mono-acid reacting with a mono-alcohol forms an ester which cannot give rise to a new condensation and the "*functionality*" of the acid or alcohol is nil in each case.

$$R{-}CO\,OH + R' \,.\, CH_2OH \longrightarrow R{-}CO\,O\,CH_2{-}R' + H_2O$$

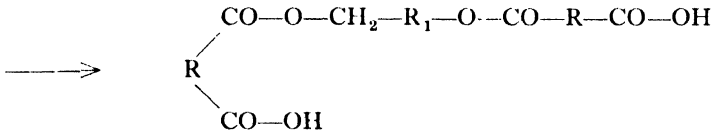
A dibasic acid, however, reacting on a dialcohol can give rise to bodies still possessing a certain functionality, i.e. a certain ability to react further.



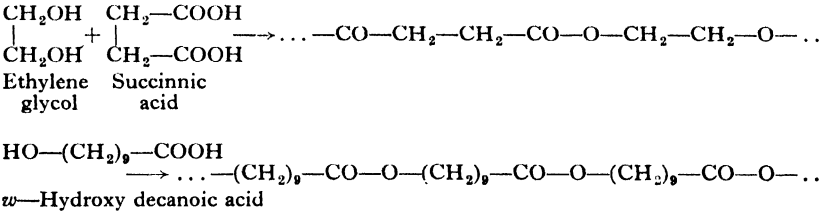
or with two molecules of dialcohol.



or again if the diacid is in excess



Carothers and Arvin[8] showed that polymeric esters may be formed either by the reaction of glycols with dibasic acids or by the self-esterification of hydroxy-acids. They found that when the number of atoms in the structural chain unit was seven or more, only polymeric products could be isolated. In the products which they obtained the molecular weights ranged from 2,000 to 5,000 and no evidence of acidic properties could be observed, indicating that the end groups were not formed of carboxyl groups. A typical example was ethylene succinate, formed from succinic acid and ethylene glycol. The average observed molecular weight was about 3,000. The product was definitely crystalline and had a melting point of 108°, but the M.P. was not sharp and depended somewhat on the rate of heating.



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + \begin{matrix} CH_2{-}COOH \\ | \\ CH_2{-}COOH \end{matrix} \longrightarrow \ldots{-}CO{-}CH_2{-}CH_2{-}CO{-}O{-}CH_2{-}CH_2{-}O{-}\ldots$$

Ethylene glycol Succinnic acid

$$HO{-}(CH_2)_9{-}COOH \longrightarrow \ldots{-}(CH_2)_9{-}CO{-}O{-}(CH_2)_9{-}CO{-}O{-}(CH_2)_9{-}CO{-}O{-}\ldots$$

w—Hydroxy decanoic acid

Fig. 227. Examples of polyesters

Polyesters. Carothers' earlier work on polycondensation appeared at the time to have purely academic significance.[7] It was, of course, a stepping-stone towards the production of nylon. At the time, the polyesters themselves had little practical significance. However, in recent years, that position has completely changed. It has been found possible to confer rubber-like properties on these linear high-polymers. The general idea is to make molecules of considerable length and flexibility of such a nature that they will remain amorphous, that is to say, they will not take up any definite crystalline pattern or structure, and then to give them some cross links at suitable intervals.

Polyesters are prepared quite simply from materials such as ethylene glycol, propylene glycol, etc., on the one hand, and succinic acid or sebacic acid on the other hand. All the polyesters give rubber-like substances when they are set or vulcanised by heat in the presence of benzoyl peroxide.[13]

The polyesters which are formed generally resemble rubber and can be handled in a similar manner. There are already a number of proprietary materials available. A variety of ingredients can be incorporated into them to produce desirable characteristics. The polyesters can be mixed in the usual way on mixing rolls which, however, should be used as cold as possible. Fillers such as calcium carbonate, iron oxide, etc., may readily be incorporated and greatly reinforce the material. By such additions tensile strength up to 3,000 lb. per sq. inch has been obtained with vulcanised polyesters. Neither carbon blacks nor materials such as zinc oxide and magnesia can be used because they have adverse effects on the products. The vulcanised products show good resilience characteristics and are very effective as substitutes for rubber in some fields of application.[19]

It has been shown that the higher the molecular weight, the higher the ultimate tensile strength.

Great things are expected in this field of activity as more experience is gained with them.

The Molecular Still. Subsequently Carothers and Hill[9] developed the molecular still which was then applied to this work. This enabled them to carry polymerisation much farther forward; by means of this, for example, polymeric esters with molecular weight of 5,000 could be converted into polymers with a molecular weight of 25,000. In this way super polymers were obtained which were tough, opaque solids, which could be melted at high temperature to give transparent viscous liquid from which threads could be drawn. These threads, when cool, could be pulled out to several times their original length. The cold drawn fibres were transparent, and had a high gloss contrasting with the opaque dull fibre drawn from the molten material. They were much stronger and more elastic, being tough and pliable, whereas the straight fibres were inelastic and weak. These drawn fibres were far superior to rayon. They gave a fibre pattern under X-ray examination which indicated considerable orientation parallel to the fibre axis. The X-ray patterns of the undrawn fibres showed that although they were crystalline, the crystals were orientated at random.

Little force is required to effect the drawing action. The new dimensions are permanent properties of the drawn fibre. It is stable in this form and unless brought to high temperature and melted, it will not return to the undrawn disorientated condition.

Carothers and Van Natta[10] studied the behaviour of ω-hydroxydecanoic acid which when heated formed polyesters of the same general structure.

Similar methods to those used in the preparation of the polyesters enabled the preparation of a polyamide from ε-aminocaproic acid. A molecular weight value of about 1,000 was found for one of the lower polymers, but no values were obtained for the higher products prepared in the molecular still. This product was insoluble in common organic solvents with the exception of hot phenol and hot formamide. It had the cold drawing fibre characteristics previously observed.

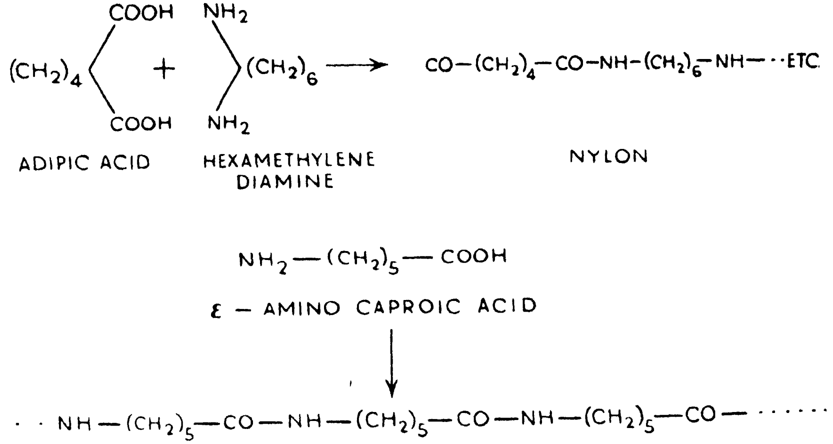


Fig. 228. Formation of polyamides

The Discovery of Nylon. Up to this stage all the work was purely fundamental, aimed at ascertaining more facts about polymerisation. However, some of the facts obtained about these fibres suggested there were possibilities from the commercial angle. It is rather startling to realise that at this stage the work was almost abandoned. The difficulties confronting the endeavour to prepare fibres on a large scale from these materials appear to be insuperable. At this stage Carothers directed his work almost exclusively to the development of products based on the polyamides. He made polyamides from a variety of amino acids and from dibasic acids and diamines. In 1935 he prepared a product from hexamethylene diamine and adipic acid. He found that fibres could be made from this polyamide by drawing a thread from the molten material. The undrawn fibres were found to undergo a remarkable change in physical properties when cold drawn. They had high tensile strength and elasticity. They were insoluble in common solvents, and had a high melting point of 263°C. It was decided to base the initial manufacturing operations on this material since it seemed to have the desirable characteristics. For some time after this, in spite of considerable work on other combinations no other polyamide was found to be as good as this. It is still the leading type. From that time onwards the problem was more one of engineering and developing the right conditions for preparing and handling the material. These problems have been very successfully solved, so that at the present time the annual output of nylon in the United States has mounted to the order of 100 million pounds per year.

Many different dibasic acids, diamides and amino-acids may be used to make polyamides.

TABLE 153

TYPICAL POLYAMIDES

Components	Polyamide	M.P. °C.
Hexamethylene diamine + adipic acid	Polyhexamethylene adipamide	248
Decamethylene diamine + adipic acid	Polydecamethylene adipamide	230
Pentamethylene diamine + sebacic acid	Polypentamethylene sebacamide	195

Further variations are possible by copolymerisation of these. Evidently an unlimited number of products is available. They will vary in melting point, solubility, flexibility and so on.

There are two methods to produce polyamides:[1]

(*a*) either from diamines with at least one free H-atom attached to each amino-group and dicarboxylic acids or their derivatives, or

(*b*) from ω-amino-carboxylic acids, their lactams or derivatives.

Diamines used are tetra-, penta, -hexa-, deca-methylenediamine, and acids such as adipic, pimelic and sebacic acid.

Standard production proceeds along the following lines. On heating, a salt is formed first, which condenses at 190° to 300°C. The reaction is accelerated by continuous removal of the formed water or alcohol. It is recommended to work in an autoclave under pressure at higher temperatures in an inert gas to avoid discoloration at temperatures above 220° C. Catalysts are generally unnecessary, although solvents (phenols) are sometimes advantageous.

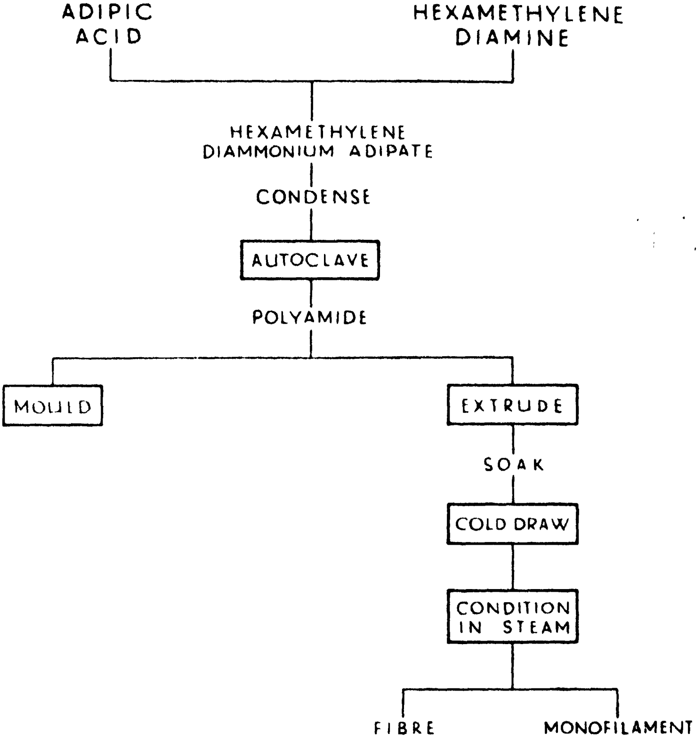


Fig. 229. Flow sheet for polyamide products

A typical example is the following:[5] 26·4 parts of hexamethylenediamine, 33·2 parts of adipic acid, 60 parts of xylenol mixture (boiling range 218°–223° C.) are heated for 7 hours at 218° C. The reaction mixture is poured into alcohol, when the precipitated polyamide forms a white crystalline powder, M.P. 250° C.

To obtain pale-coloured products, the use of vessels made of glass, silver, chromium, etc., and absence of oxygen is indispensable. Polyamides with good solubility are particularly valuable. Innumerable variations are possible by mixing various diamines with different dicarboxylic acids. Other variations may be obtained by using polyamides with olefine or acetylene links or with —O— or —S— bridge.

The Production of Nylon. The manufacture[17] of the leading type of nylon is based on two chemical intermediates, adipic acid and hexamethylene diamines; both of them derived from coal, being made by high pressure synthesis from coke-oven gases and coal-tar intermediates.

Solutions of adipic acid and hexamethylene diamine are reacted in a stainless steel kettle to form hexamethylene diammonium adipate. This is transferred into a cylindrical autoclave heated by coils and maintained under controlled conditions. Stabilisers are added to control the molecular weight and viscosity of the product. Polymerisation takes place and a long chain linear polymer is formed with a molecular weight which is much higher than 10,000. Molten viscous nylon is formed in this way, and is then allowed to flow on to a broad slowly revolving aluminium wheel. A shower of water sets the material to a milky white ribbon which is cut by a rotary cutter into flakes. This is the commercial material, and the form in which it is generally handled. In the production of filaments the flake is allowed to fall on to a specially heated grid on which the polymer melts. The molten nylon passes through this grid into a funnel-shaped chamber which leads into the spinnerette assembly. Specially designed pumps are used to carry it

Fig. 230. Molten nylon emerging as monofilaments from the extrusion head. The monofilaments solidify as soon as they make contact with the quenching bath[20]

through here. It is first passed through a hot sand filter bed which ensures smoothness and purity of product. It then passes to the spinnerette which consists of a thick disc of metal, 2 inches in diameter. This is pierced with fine holes which flare out into tiny funnels at the upper end where the polymer enters. The pumps cause the molten nylon to be extruded through the apertures; as soon as they go into the air the filaments harden and are carried off at high speed, up to 2,500 yards per minute. The filaments pass through a three-sided chimney, in which a draught of air further cools them. They then pass into a steam jacket which moistens the filaments and causes them to stick together, making them more convenient for handling. At this stage the filaments do not show the outstanding characteristics of the material. It is necessary to draw the filaments out to about four times their original length; each filament acquires a smaller diameter, becomes highly orientated, and has a completely different physical structure.

Filaments of the finest diameter as low as anything available in real silk may be prepared in this way. A one denier filament of nylon has a diameter of about 1/2500 inch. A denier fibre is defined as one of which 9,000 metres weighs one gram.

Although the possibilities of making separate types of nylon are infinite, very few combinations of suitable acids and diamines have been found. In fact, the practical field has narrowed down to a few raw materials. For example, the acids which are of leading importance are adipic acid and sebacic acid. The outstanding diamines are hexamethylene diamine and decamethylene diamines.

Adipic Acid. Adipic Acid is made by a catalytic hydrogenation method from phenol.[2] Phenol is hydrogenated simply and smoothly to cyclohexanol. This is then oxidised to adipic acid. The actual material is a white crystalline solid melting at 148°C. Although most adipic acid is obtained from phenol, it is possible to make cyclohexanol from cyclohexene. The latter material is available from waste petroleum products, and offers a potential source of supply of adipic acid.

The Germans claimed to produce adipic acid by a much cheaper process. Aqueous tetrahydrofuran is passed down through a nickel catalyst in a tower and meets a stream of carbon monoxide at 200 atmospheres and 250°C. Adipic acid is formed in high yield. It is much cheaper than when obtained from phenol.

Sebacic Acid. In this instance the raw material is a vegetable oil, namely, castor oil. It is surprising what a strong influence castor oil has in the plastic industry. When castor oil is fused with caustic soda it is broken down substantially into sebacic acid. Improved methods have latterly been developed, one of which involves a high pressure treatment of castor oil and gives a much higher yield of pure sebacic acid.[6]

Diamines. The diamines employed in the production of nylon are themselves derivatives of the acids previously considered. They have been evolved as a consequence of the work on adipic and sebacic acids, etc.

According to one method a mixture of ammonia and adipic acid is

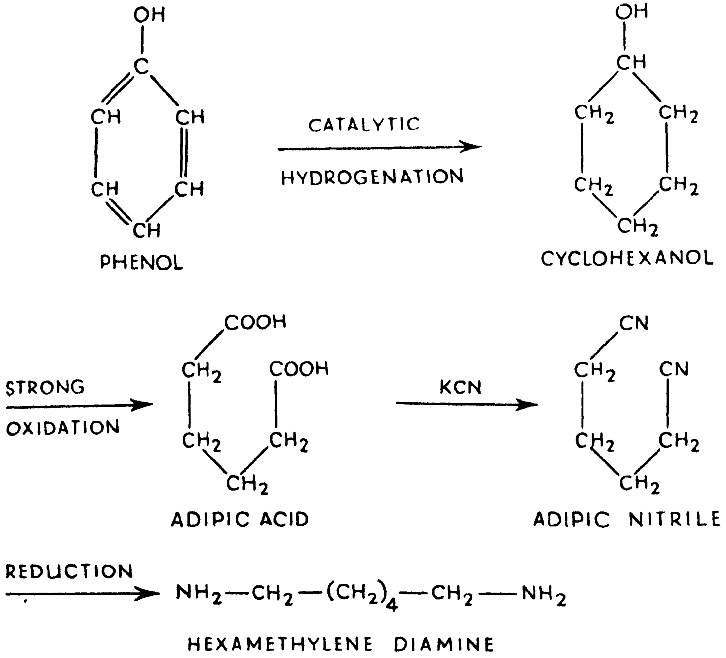


Fig. 231. Formation of hexamethylene diamine

passed over a dehydration catalyst at high temperature and gives adipic nitrile. This can be catalytically hydrogenated under high pressure and gives a very high yield of hexamethylene diamine. This is a white solid, melting at 30° C. Decamethylene diamine is produced along somewhat similar lines from sebacic acid. It is a white solid melting at 60° C.

Properties of Nylon. Nylon is available in the form of tough, horn-like, translucent, white chips. The melting point will depend on the type of nylon. However, the commercial types are comparatively few in number, the outstanding one being that produced from adipic acid and hexamethylene diamine. This has a melting point of 250° C., softening only a few degrees below this. When heated up to melting point in contact with the air it tends to oxidise and becomes brown. It burns with some difficulty and for all practical purposes can be regarded as non-inflammable.

Nylon is extremely resistant towards solvents. It is unaffected by nearly all organic solvents. It is impervious to all dry cleaning solvents. It may be taken up into solution in phenol, cresol, in formic acid, acetic acid and strong mineral acids. Such solutions may then be diluted with ordinary organic solvents, such as toluene, etc. The specific gravity is 1·08. Nylon is insoluble in water. It is not attacked by alkalis, either weak or strong. Strong mineral acids cause it to break down and hydrolise. It is quite unaffected by fungi and bacteria. The molecular weight of available nylons ranges between 7,000 and 20,000. It has a refractive index of 1·53.

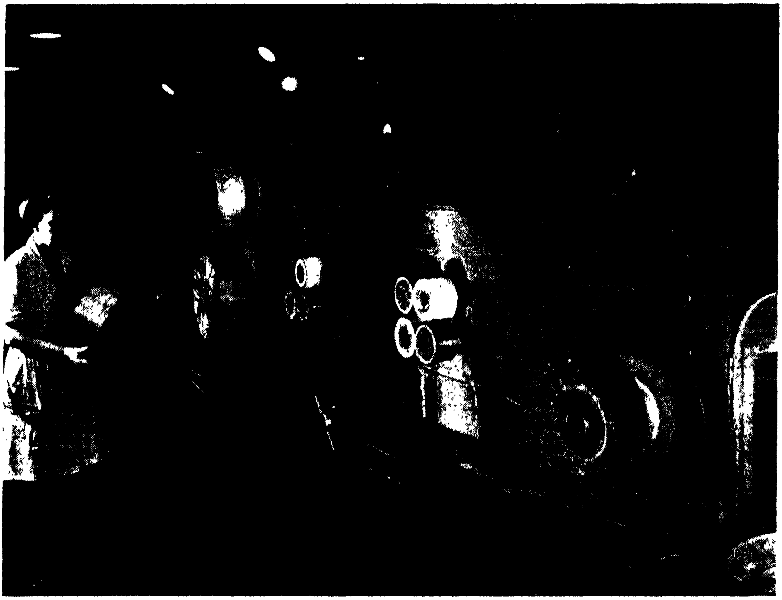


Fig. 232. The extruded nylon is being drawn to about four times the original length in order to orientate the molecules and thus develop the maximum strength of the fibre[20]

Properties of Nylon when Cold Drawn. The outstanding characteristics of nylon is the behaviour when it has been cold drawn. It is capable of being drawn to seven times its original length, although in practice it is drawn to four times. When drawn to this extent it shows remarkable flexibility and elastic properties. All nylon monofilaments are drawn after they have been formed. They are soaked in water and then drawn to four times the elongation at a rate which may be 500 feet per minute. The filaments are then steamed for some hours to stabilise them.

Tensile strength of nylon is ordinarily about 7,500 lb. per square inch. Yet a filament 0·021 inches diameter when cold drawn has tensile strength of 58,500 lb. per square inch dry, dropping only to 43,000 lb. per square inch when immersed in water. Elongation is about 35 per cent ordinarily, increasing slightly when cold drawn. The filaments show 93 per cent recovery when deformed.

The behaviour towards moisture is also profoundly influenced by the drawing treatment. When cold drawn the tensile strength when the material is wet is very little less than the dry strength, something of the order of 90 per cent. Such drawn fibres are superior to silk in this respect. They are quite as resistant as natural silk towards sunlight and ultra-violet light. Nylon burns very slowly. It shows no tendency for ageing.

Nylon filament has exceptionally good resistance to abrasion, and articles made from it wear well. This toughness is one of the outstanding characteristics which is well illustrated in the leading applications in the form of monofilament for bristles. These are not only used for personal use as tooth brushes and hair brushes, but also for industrial brushes. Nylon is not inflammable to anything like the same degree as any of the cellulose materials; in a hot flame it melts and ultimately burns quietly.

The resistance of nylon to solvents makes it of great interest as a fibre for textiles, since these can be handled for cleaning with any of

TABLE 154

ELECTRICAL PROPERTIES OF NYLON

R.H. = Relative Humidity

	Moulded	Cold Drawn
Volume resistivity—ohm/cm., 18% R.H.	10^{13}	4×10^{14}
50% R.H.		$1·6\times 10^{13}$
Dielectric constant—50 cycles, 0% R.H.	3·2	—
10^3 cycles, 0% R.H.	—	4·5
10^6 cycles, 50% R.H.	3·3	6·3
10^3 cycles, 0% R.H.	3·6	—
Power factor, 50 cycles, 0% R.H.	1·0	—
10^3 cycles, %0 R.H.	1·5	2·7
10^3 cycles, 50% R.H.	—	11·7
10^6 cycles, 0% R.H.	2·2	—
Dielectric strength, v per mil., 50% R.H.	—	490

the normal cleaning solvents. In many industrial applications such as bottle washing, textile printing, dry cleaning, salvage disposal, etc., nylon has proved many times more durable than natural bristle. Nylon dissolved in formic acid can be cast into sheet and foils.

Dry nylon has excellent electrical characteristics and is used for coating wires used in electrical equipment.

Fig. 233. Hanks of nylon monofilaments after passing through the drying oven[20]

There is already much activity in modifying the characteristics of nylon by introducing other resins. For example, stiffness is a desirable feature of bristles. Some phenolic resins are found to be suitable for combining with nylon. A typical example is the following from a Du Pont patent:[12]

678 parts of hexamethylene di-ammonium adipate were intimately mixed with 146 parts of a p-hydroxydiphenyl-formaldehyde resin, and charged into a stainless steel autoclave. During a two-hour period the autoclave was heated to an internal temperature of 270° C., the pressure rising to 250 lb. per sq. inch. During the next half-hour the pressure was reduced to atmospheric by permitting the water of the reaction to escape, following which the autoclave was maintained at an internal temperature of 270° C. for an additional hour. The modified polyamide thus obtained was then extruded from melt in bristle form.

The bristle was yellow in colour and softened at 200°–230°C. It had a modulus of elasticity (measure of stiffness) of $0{\cdot}37 \times 10^6$ for modulus of elasticity and 7·6 per cent for water absorption for unmodified polyhexamethylene adipamide bristle.

Nylon Fibre Compared with Silk. Hoff[15] has given some interesting information about the behaviour of nylon fibre by comparison with silk and rayons. Nylon has high elastic recovery, far superior to silk or rayons. Stretched 4 per cent, held for 100 seconds and then released nylon had fully recovered after one minute, whereas silk and acetate rayon had only returned 50 per cent, while viscous rayon had only returned 30 per cent.

The superiority from the point of view of water absorption is also clearly marked. At 60 per cent relative humidity nylon takes up 3·5 per cent moisture. Acetate rayon takes up 6·5 per cent, silk takes up 11 per cent, viscose 12 per cent, and wool takes up 13 per cent water. Perhaps more important is the fact that nylon retains almost 90 per cent of its tensile strength when wet, which is well in excess of the net strength of wool, and incomparably superior to the rayons.

In Germany the material known as Igemide B (or Perlon L), based on amino capro lactam, was mainly used for spinning.

Nylon yarns are currently being supplied with a dry tenacity of about 5 grammes per denier, with an elongation of 23 per cent at the break. This is half again as strong as silk with the same elongation. It is about half again as strong as steel, weight for weight. Nylon yarns can be produced with a tenacity approaching 9 grammes per denier, still having good extensibility. For weaving and hosiery a strength of 5 grammes is adequate. Nylon is remarkably clean and free from broken filaments. For hosiery, nylon is the most elastic yarn yet known, fibres stretched 4 per cent recovering immediately the tension is released. It is this resilience which has made nylon yarn so suitable for hosiery. Current weaving yarn is supplied as 45 denier with 13 or 15 filaments, equivalent to three-thread silk in the gum, on bottle bobbins, or cheeses.

Woven Nylon. Woven nylon can be shaped to any desired permanent dimensions by being subjected to heat and pressure over a suitable mould.

Woven nylon is extensively employed at the present time for mosquito netting. There appears to be a big future for the material in the form of woven screens. Woven strip is already extensively used for upholstery, etc., in public transport vehicles.

Hoff[16] has recently proposed the use of nylon strands to form the fabric used in rubber tyre carcasses instead of the cotton cords now used. Nylon was asserted to have greater strength, flexibility and elasticity,

Moulding of Polyamides. Up to the present time not much has been heard about moulding polyamides. The output of the material until recently had not been able to keep up with the demands for fibres and filaments. A certain amount of work has, however, been done on moulding, both by compression and by injection. Articles such as bobbins, combs, beakers, and so on, are being produced in large quantities. For the time being work has had to be confined to the straight material without additions. This is due to high softening point, which makes mixing very difficult. Moulding conditions will likewise require the ability to use high temperatures. Moulded articles have the valuable combination of properties, namely, high temperature resistance together with great toughness. Such mouldings are being used for flexible spools and coil formers. They are also going into zip fasteners. Mouldings can be dyed after moulding by immersion in hot solutions of dyestuffs. Parts can be cemented together by using cresol or phenol.

Efforts have been made to use the material by injection moulding.

Injection Moulding of Nylon. Although at the present time nearly all nylon is used for fibres or filaments, much consideration has been given to the possibility of moulding. Considerable progress has been made in the injection moulding of nylon. Moulding equipment must be able to work at higher temperatures, e.g. of the order of 280° to 320° C., because of the high softening point of nylon. Stainless steel equipment is found to be suitable. Nylon melts very sharply, changing rapidly from solid to liquid. There is not the usual plastic range shown by other thermoplastics. Because the material is so fluid special injection nozzles have been designed and dies must be even more carefully constructed than in the ordinary way.

The material has a high moulding shrinkage of 0·012 ins. per in., a fact which must also be considered in the designing of the dies. Because the material is so fluid at the injection temperatures, the injection pressures employed can be quite low, of the order of 2 tons per square inch.

In changing from the molten state to the set chilled condition there is a contraction of 16 per cent. Consequently it is essential to maintain pressure for a short time after injection to take up the contraction. So that the procedure as carried out at the present time is to have a cycle of about 30 seconds of which half is time occupied maintaining pressure on the moulding. At the present time moulding is still confined to comparatively thin sections.

Moulded nylon has a number of attractive properties. It has a high tensile strength combined with a horny and resilient character. Since there is no orientation developed the tensile strength is not comparable with that developed in drawn filament. It is extremely resistant to abrasion and has high impact strength. Perhaps of outstanding importance is the fact that the softening temperature is the highest available among the thermoplastic materials. It should not be held above 135° C. under load. Moulded polyamides have recently been considered by Rahm[11].

The mouldings are of course extremely resistant to chemicals and solvents, being affected only by such materials as phenol, cresol and strong mineral acids. The chief disadvantage is the water pick-up.

Identification of Nylon. Identification of nylon fibres is now clearly desirable. According to Gerber and Lathrop,[14] a quick way of distinguishing between cellulose acetate and nylon, is to apply the acetone solubility test. Cellulose acetate readily dissolves, while nylon is insoluble in this agent. Cellulose acetate also dissolves in cold glacial acetic acid, whereas nylon only dissolves in the hot acid and forms a thick white gel on cooling. Nylon differs from regenerated cellulose (viscose) in being insoluble in calcium isothiocyanate solution (s.g. 1·36) at 70° C. Natural protein materials like casein and wool give a characteristic brick-red colour with Millon's reagent, but nylon fibres only acquire a faint yellow tinge when the solution is boiled. In contact with iodine solution nylon forms a characteristic brown to black stain which cannot be removed by washing. Burning nylon fibre has a smell reminiscent of burning celery or green beans.

Elastic Nylon. Recent developments in the polyamide field have led to the production of elastic products. One type, known as Isobutyl 610, can be stretched from 250 to 400 per cent elongation. The elastic recovery is from 95 to 99 per cent, far in excess of ordinary nylon.

Polyurethane. Very attractive materials have been produced in Germany having much in common with polyamides.[11]

After Carother's studies of the superpolyamides became known, I.G. Farben began investigations along similar lines, and developed polyurethane polymerisation. It found that long-chain aliphatic diamines and aliphatic diisocyanates yield only infusible and strongly hydrophilic polymers, the polyurethanes unsuitable for use in fibres or plastics. The linear polyurethanes proved to be very versatile plastics with some properties superior to those of the polyamides. The easiest to produce industrially is the polyurethane made from 1,6 hexanediisocyanate, and 1,4 butylene glycol; it is suitable for the production of fibres, plastics, and especially bristles.

The reaction between one mol of each of the two compounds in a solution of monochlorbenzene takes about one hour, and the polyurethane separates as a fine sandy powder in practically quantitative yield. By controlling the temperature and other reaction factors, polyurethanes of varying degrees of polymerisation can be produced. Polyurethanes have been recently discussed by Bayer.[3]

Hexamethylene diamine is treated with phosgene when di-isocyanate is formed.

$NH_2.(CH_2)_6.NH_2 + 2COCl_2 \longrightarrow OCN.(CH_2)_6.NCO + 2HCl$

Di-isocyanate is reacted with butandiol produces a linear polymer, m.p. 170°–180° C.

Monthly production in Germany was: 330 tons Igemide B, 40 tons Igemide A, 5 tons Igemide U. It was allocated in the following way: tyre yarn, 100 tons; parachute yarn, 133 tons; parachute braid, 20 tons; special yarn, 50 tons; insulation, 9 tons; bristles, 100 tons.

TABLE 155

MELTING POINTS OF SOME POLYURETHANES

Number of carbon atoms in:		Melting point °C.
Diisocyanate	Glycol	
4	4	190
4	6	180
4	10	170
6	3	167
6	5	159
5	9	147
12	12	128

Synthetic Plastics and Fibres. The polyurethanes are marketed as Igamid U with a K-value of 60–70 for plastics, and as Perlon U with a K-value of 55–60 for synthetic fibres and bristles. Perlon U has a low melting point, practically as low as that of acetate rayon, and this factor makes it unsuitable for a number of textile applications. It may be spun in air to form threads which are led into a water bath at 80°C. The threads are chemically wet and take up no water. The strength of polyurethane fibres and bristles is practically equal to that of the super-polyamide products. Laboratory tests show that polyurethane threads can be produced which surpass the strength of the best natural silk. Tests showed 7·5 g/denier against 3·5 g/denier for silk.

One specific characteristic of Igamid U and all other polyurethanes is their low water absorption.

The polyurethanes also surpass the polyamides in electrical properties, weather resistance, and resistance to acids. These special properties, together with others characteristic of the polyamides, make Igamid U a valuable high-melting thermoplastic for moulding applications.

Perlon U, with its hardness, wirelike elasticity, and insensitivity to moisture up to 80°C., is a valuable material for bristles. It differs from the polyamides in dying properties as it contains no basic groups. It can only be dyed with acetate-rayon or suspension dyestuffs; whereas nylon must be dyed with acid dyestuffs. Because of the absence of basic groups, melted Igamid U is much less sensitive to atmospheric oxygen than the polyamides and will not darken during melting, extrusion, or spinning even if the machinery is not completely airtight.

TABLE 156

PROPERTIES OF THE IGAMIDS

Property	Igamid U (Polyurethane)	Igamid A (Polyamide)	Igamid B (Polyamide)
Specific gravity	1·21	1·14	1·15
Melting point, approximate, °C.	183	255	210
Brinell hardness, kg/cm.^{2}	750	1000	600
Flow temperature, °C.	170–180	220–225	160–180
Impact strength, cm.–kg./cm.^{2}	ca. 100	>100	—
Unoriented material			
Tensile strength, kg./cm.^{2}	620	—	380
Resistance to cold, °C.	+8	—	+13
Oriented material			
Tensile strength			
Machine direction, kg./cm.^{2}	874	—	1,050
Cross direction, kg./cm.^{2}	400	—	860
Elongation			
Machine direction, %	60	—	73
Cross direction, %	81	—	70
Resistance to cold, °C.	−30	—	−30

A few other types of polyurethanes also offer promise of industrial importance. The polyurethane of 1,4 butanediisocyanate and 1,4, butylene glycol has practically the same properties as Igamid U, but melts at 194°C., 12° higher than the latter. It will probably be cheaper than Igamid U, and because 1,4, butylene glycol is synthesised from acetylene and hydrogen cyanide, be independent of phenol or benzene. These simple homogeneous polyurethanes are completely insoluble in all solvents at low temperatures and are only soluble in a 90 : 10 mixture of phenol and water. The mixed polymers, produced from a mixture of glycol and diisocyanate components, have good solubility in chlorinated hydrocarbons even at low temperatures, have lower melting point, greater ranges of thermoplasticity, greater softness, and better compatability with plasticisers, and are therefore ideal for use in films, foils, and leather substitutes.

Igamid UL, a mixed polyurethane proposed as a leather substitute, is obtained by melting together one mol of 1·6-hexanediisocyanate, 0·5-mol of 1,4-butylene glycol, and 0·5-mol of methylhexanediol. It is a very soft material and is superior to leather in many respects.

Moulded Plastics and Plastic Foams. For the production of moulded plastics, diisocyanates are mixed with polyhydroxy compounds in molar ratios, together with large amounts of fillers such as wood flour. The reaction takes place under heat and pressure, as with phenolic resins. Only slowly reacting diisocyanates with high melting points, such as those prepared from dianisidine and di-p-xylidinemethane, can be used to avoid premature reaction. Good results are obtained by combining these with a polyester containing many free hydroxyl groups, which has been prepared from adipic acid and trimethylolethane.

At temperatures of about 140–160°C. and moulding times of about 5–10 minutes, moulded products are obtained which surpass the cured phenolic plastics in many respects, although somewhat more thermoplastic at higher temperatures. Their main advantages are: high alkaline resistance; high electrical resistance (about 3–5 million megohms); high arc resistance, even when wet; much better flow than the phenolics; and high elasticity and impact strength.

Insoluble acetate rayon can be formed by use of diisocyanates.

Plastic foams of high strength can be prepared from the polyurethanes. When a diisocyanate is mixed with a polyester prepared from a dicarboxylic acid and a trihydroxy alcohol and containing free hydroxyl and carboxyl groups, reaction begins at 50°C. with the formation of urethane and acid amide linkages and the splitting off of carbon dioxide. This causes the tough substance to raise like dough and harden as the cross-linking progresses. Besides having high strength, these foams can be produced in any desired elasticity. They are considered highly superior to balsa wood and urea foams as structural materials.

Polyurethanes have proved to be outstanding adhesives for attaching rubber and synthetic rubbers to any surfaces including iron, light metals, porcelain, etc., yielding heat resisting joints. The polyurethanes prepared with m-tolylenediamine and hexa methylene diamine were exceptionally good. These are the Desmodur adhesives.

The intermediates required for the production of the urethanes are diamines, phosgene, glycols, and polyhydroxy compounds. For the production of the linear polyurethanes, mostly 1,4-butylene glycol and methyl-1,6-hexanediol are used. The intermediates required for the production of the urethanes are diamines, phosgene, glycols, and polyhydroxy compounds. For the production of the linear polyurethanes, mostly 1,4-butylene glycol and methyl-1,6-hexanediol are used. The intermediates for the diisocyanates are the corresponding aliphatic and aromatic diamines which are converted into the diisocyanates by reaction with phosgene. Among the straight-chain diamines, 1,6-hexamethylenediamine is easily available by hydrogenation and adiponitrile. Acrylonitrile adds another mol of hydrogen cyanide in the presence of alkaline catalysts, and the resulting succinonitrile can be hydrogenated to give 1,4-diaminobutane. There are several methods for the conversion of aliphatic diamines into diisocyanates with two benzene rings are not distillable. However, after the reaction with phosgene, they separate from the chloro-benzene in some cases practically quantitatively.

The cost of the polyurethanes will be about the same as that of the polyamides. Polyurethane leather can probably be marketed cheaper than the competitive polyamide brands. The production cost of the aromatic diisocyanates is such that even high-grade lacquers and moulding compounds which contain only a small percentage of diisocyanates will not be too expensive.

REFERENCES

1 AKIN AND TEAGARDEN. *Modern Plastics*, 1943, November, p. 115.
2 ARONOV. U.S.P., 2,191,786.
3 BAYER. *Angew. Chemie*, 1947, **59**, 257.
4 BOLTON. *Chem. and Ind.*, 1942, **60**, 31.
5 British Nylon Spinners, Ltd., B.P. 552,190.
6 BRUSON. U.S.P., 2,182,056.
7 CAROTHERS. *High Polymers*, Vol. I, Interscience Publishers Inc. New York, 1940.
8 CAROTHERS AND ARVIN. *J.A.C.S.*, 1929, **51**, 2,560.
9 CAROTHERS AND HILL. *J.A.C.S.*, 1932, **54**, 1,566.
10 CAROTHERS AND VAN NATTA. *Chem. Ref.*, 1931, **8**, 253.
11 DE BELL, GOGGIN AND GLOOR. *German Plastics Practice.* U.S.A., 1946, p. 300.
12 Du Pont de Nemours. B.P. 461,237/1937; B.P. 474,999/1938; B.P. 487,734/1938; B.P. 490,922/1938; B.P. 494,236/1938; B.P. 506,125/1939; B.P. 545,940/1942; U.S.P. 2,181,140.
13 FULLER AND BRIGGS. *Rubber Age*, 1943, **24**, 525.
14 GERBER AND LATHROP. *American Dyestuffs Reporter*, September 2, 1940.
15 HOFF. *Ind. Eng. Chem.*, 1936, **32**, 1.560.
16 HOFF. U.S.P. 2,317,911/1943.
17 NYLON MANUFACTURE. *Chem. Met. Eng.*, 1943, **50**, 91.
18 RAHM. *Plastics* (U.S.A.), 1948, **8**, 21
19 SUMNER AND MYERS. *Rubber Age*, 1943, **24**, 525.
20 Photographs by courtesy of Imperial Chemical Industries, Ltd.

CHAPTER XXVII

ALKYD OR GLYPTAL RESINS

CAROTHERS described thermoplastic materials having long chain linear molecules formed by the reaction of the glycols with dibasic acids. When glycerol is substituted for the glycol very different resins are obtained, the behaviour of which is quite different from the polyesters. The resins formed are known as *alkyd* or *glyptal* resins. These resins long preceded the polyesters by many years.

Alkyd resins, or glyptals, as they are also known, form one of the most important groups of synthetic resins. The amount used is as great as the amount of phenol-formaldehyde resins. There are a number of proprietary types available. Although, strictly speaking, they are not generally used for the normal run of plastic manufacture, for example, by moulding, by casting, and so on, they are of outstanding importance in the field of coatings. One gets some impression of their importance by consideration of some of the leading applications. Coatings based on glyptals are used for:

1. Air drying enamels for interior and exterior.
2. Tin coating.
3. Printing inks.
4. Stove enamels.
5. Metal primers and finishes.
6. Car finishes.
7. Coated fabrics.
8. Aircraft lacquers.
9. Marine paints.

Flexible types of alkyd resins are available, which have sound and vibration absorbing properties and find applications as gaskets and packings. Alkyd resins have good electrical properties and are used widely in the electrical industries.

Essentially, they are made by the formation of esters from polybasic acids with polyhydric alcohols. The prototype is the reaction between phthalic anhydride and glycerol. Apart from the straightforward materials formed on this basis, there are numerous modifications which have wide application in industry. Among these may be mentioned alkyds modified with phenolic resins, urea resins, etc., alkyd resins modified by drying oils, and alkyd resins modified by natural resins.

Historical Background. The formation of a resin from glycerine and phthalic anhydride was discovered by Smith[10] in 1901. No great progress was made for a number of years, until a group of patents were taken out about 1914, under the auspices of the General Electric Company of America. Among these was a practicable method of preparing phthalic anhydride from napthalene, the absence of which had previously been the main obstruction to any development. Commercial materials began to become available in 1926, and thereafter an ever-growing series of products appeared. Much of the knowledge of these materials has been based on the work of Kienle, who has contributed greatly towards the present-day understanding of resin formation.

Leading Raw Materials. The principal raw materials for the production of alkyd resins are glycerine and phthalic anhydride.

Glycerine. Glycerine is one of the chief organic chemicals at the present time. It is used in numerous industries. During the war, by virtue of its large-scale usage for the production of explosives, it is in extremely short supply. A by-product of the soap industry, it is manufactured on a very large scale. Latterly, a synthetic method of production has been developed from petroleum wastes via propylene.

U.S. production of glycerine is about 200 million pounds, of which in 1944, 36 million pounds were used in plastics.

Glycerine is ordinarily a thick, viscous liquid which is extremely hygroscopic. Ordinary commercial glycerine contains 20 per cent of water. It is important to remember this fact in formulating quantities used for the preparation of resins. The specific gravity of pure glycerine is 1·2159, the purity being generally assessed by the specific gravity and by the refractive index. It is soluble in water and alcohol in all proportions. Its boiling point is at 200° C., when it begins to char.

Phthalic Anhydride. In recent years phthalic anhydride has attained considerable commercial importance for a number of steadily growing applications. Not only is it a primary material for making alkyd resins, but it is also employed in the production of the most widely used group of plasticisers, many of which are essential ingredients in most plastic compositions. In present circumstances it is in short supply owing to its application for making smokeless powders.

It is obtained in long, water-white, bulky crystals which have a characteristic aromatic odour.

Phthalic anhydride is obtained by heating phthalic acid up to its melting point of 213° C. The anhydride has a melting point of 128° C., and boils at 277° C. It sublimes readily when heated. When boiled with water phthalic acid is regenerated. At ordinary temperatures in solution no phthalic acid is formed. The parent material for phthalic anhydride is napthalene, from which it is obtained by oxidation. The naphthalene is, of course, obtained as a by-product in the distillation of coal tar.

Other Resin Ingredients. Glycerine and phthalic anhydride are the two most important constituents for alkyd resins, but they are merely typical of two types of materials. Other polyhydric alcohols are employed, for example, glycol, ethylene glycols, diethylene glycol, mannitol, pentaerythritol, etc. In the same way, other acid anhydrides, such as those of succinic acid, tartaric acid, malic acid, citric acid, fumaric acid, adipic acid, and maleic acid are also employed.[6] The latter is particularly important.

It is interesting to note that glycerine will condense with boric acid to form a water-soluble resin, which is used for pharmaceutical purposes. A point of interest about this is that this water-soluble resin may be considered as the connecting link between inorganic glasses and organic synthetic resins.

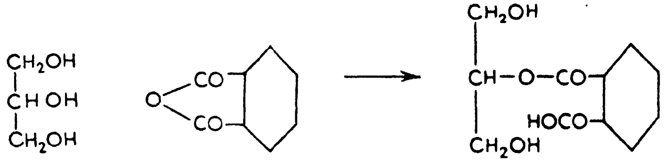


Fig. 234. Probable initial reaction between glycerol and phthalic anhydride

Preparation of the Resin. The procedure for making the straight resin is extremely simple. It is only necessary to heat the materials, no other additions being essential. Two molecular proportions of glycerine and three molecular proportions of phthalic anhydride are heated together for an hour, after which resinification begins, and a syrup is formed. With continued heating this becomes a gel. After several hours' heating a resin forms which hardens up and sets, becoming infusible and insoluble. The final setting action is rather slow even at quite high temperatures. Accelerating this has been a major problem with alkyd resins. In the intermediate stages they are soluble and thermoplastic.

Alkyd resins in the two earlier stages are soluble in many common solvents. Usually, they are dissolved in benzene, in ethyl alcohol, toluene, xylene, acetone, and other ketones, esters and ether alcohols. They are not easily soluble in aliphatic hydrocarbons. They may be saponified without much difficulty. They are non-inflammable. They fluoresce pale blue in ultra-violet light. When strongly heated they give a white sublimate of phthalic anhydride. The acid number is from 85 up to 130.

Chemistry of the Reaction. Weisberg[12] suggested that there were three stages in this resin formation, namely:

A. Fusible, soluble in acetone, affected by water.
B. Fusible, insoluble in acetone, unaffected by water.
C. Infusible, insoluble, unaffected by water.

This scheme follows the pattern suggested in the case of phenol-formaldehyde and other setting resins. As in that case it has been suggested that the first stage is the formation of a linear molecule, in this way accounting for the solubility and the heat softening characteristics.

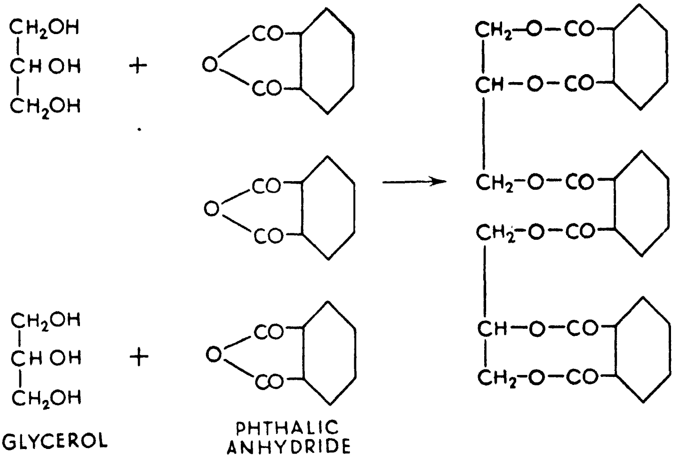


Fig. 235. Reaction between glycerol and phthalic anhydride

There are, however, still reactive groups in the molecule which can react further to yield an insoluble, infusible product. Materials so formed have been studied extensively by Kienle and his associates.[9] They found that at the beginning of reaction there was a very rapid drop in the amount of free acid present, but the disappearance of the free acid then became quite slow, continuing so until an infusible gel resulted. There was little change in rate of disappearance of free acid at the gel point.

Carothers has suggested that the reaction may be formulated in two stages, the first resulting in a linear polymer similar to that formed from glycols with dibasic acids, except that free hydroxyl groups are present; the second stage is the linking of these chains by further reaction of the hydroxyls, giving a compact three-dimensional molecule.

In the second stage, as shown, two chains such as are formed in stage one, are united by reaction of residual alcoholic groups with more phthalic anhydride. It is possible that this union might be also formed by the reaction of two groups to form an ether directly, but this appears less likely than the reaction with more phthalic anhydride, particularly since analysis of the resin just before gelation always shows the presence of unreacted carboxyl.

Weith[13] has considered the rate of increase of molecular weight for each molecule of water formed. In the first stage the net effect of one reaction resulting in the elimination of one molecule of water is to increase the length of the chain by the addition of one glycerol or phthalic acid residue, i.e. a linear molecule. The terminal hydroxyl groups in glycerol do not react to the complete exclusion of that on the middle carbon. In practice, the average length is probably not greater than six or eight glycerol-phthalate units when gelation sets in.

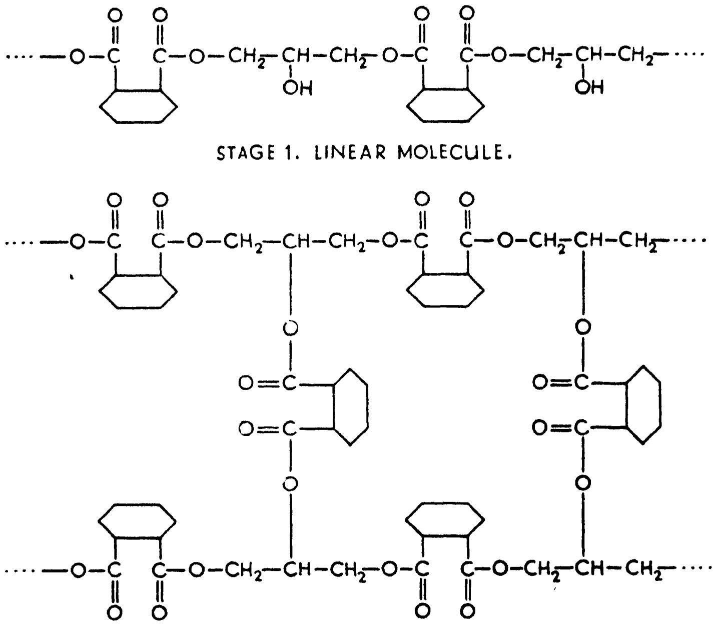


Fig. 236. Alkyd resin formation according to Carothers

On the basis of his extensive work with alkyd resin, Kienle[8] has outlined three necessary conditions for alkyd-resin formation:

1. High molecular compounds are only possible when the interacting molecules are poly-reactive. The links are chemical bonds, at least in part.

2. Interlocking proceeds by chance contact of any two reactive points.
3. The size and shape of reacting molecules and the position of reactive points determine the physical properties of the resulting polymer.

The simplest resins based on glycerol and phthalic anhydride are hard, brittle resins. Where longer chain polybasic acids are employed, e.g. adipic acid, sebasic acid, etc., the resins are flexible and tough.

Straightforward glyptals have comparatively limited applications. They are soluble in alcohol, and may be set by heating. They are employed in the preparation of stoving lacquers. They are also used as bonding agents for moulding compositions with mica. The material known as *Micanite* is of this type. Small quantities of plasticisers are sometimes employed with alkyd resins, notably tricresyl phosphate, dibutyl phthalate, triacetin, etc.

Recently Bigelow[3] has described alkyd moulding powders which are very fast curing at very low pressures. The action is exothermic and the press must close very rapidly.

Oil-Soluble Glyptals. A most important development in the subject was made about 1912, when it was found that the resins could be made oil-soluble. This fact was of such outstanding importance that for many years most activity has been devoted to the study of this angle.

This is achieved by replacing part of the phthalic anhydride by oleic acid. The resulting resin was found to be soluble in linseed oil. Arsem described the preparation of resins incorporating oleic acid.

$$\left.\begin{array}{l}\text{92 parts Glycerol}\\ \text{148 parts Phthalic anhydride}\end{array}\right\} 210^\circ\text{C.}$$

add

141 parts Oleic acid
37 parts Phthalic anhydride

After 1½ hours at 210°C. a product is obtained which is soluble in acetone; this became insoluble in 24 hours at 160°C.

The original material did not prove to be very satisfactory, because oleic acid is not a drying product. When it was replaced by an acid such as linoleic acid derived from linseed oil, an air-drying product was obtained. A further step was the introduction of the actual drying oil. Thus, linseed oil could be used, or tung oil, cottonseed oil, castor oil, and so on.

The resins produced began to show behaviour which could only be attributed to the oil. They were air-drying in the same way as the oils themselves were. In the case of tung oil, for example, it was necessary to submit the resin to similar heating procedures to those used for the straight oil. Thus, tung oil requires to be heated to 270° C., to give a product which will dry, and have the best strength durability, and so on. A similar bodying treatment must be applied to the resins.

It was found that these oil-modified resins applied as coatings dried far more rapidly than varnishes, which are, of course, natural resins taken up in drying oils.

It was found that metallic driers used in ordinary paint technique with these oils are equally effective when used with the oil-modified glyptal resins. These driers are resinates, linoleates, naphthalates of cobalt, manganese, lead, etc.

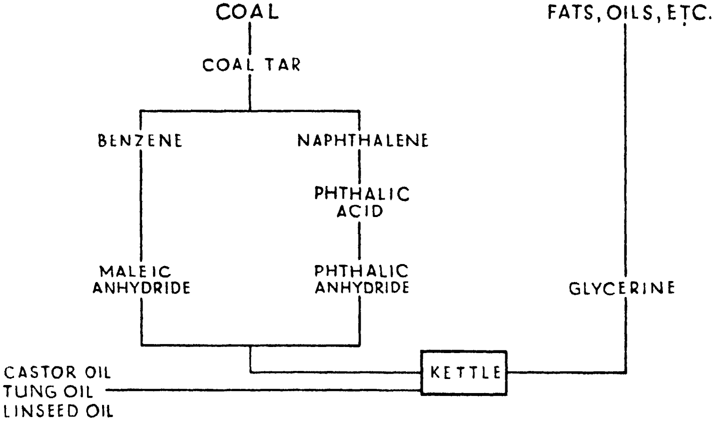


Fig. 237. Flow sheet for alkyd resins

A number of different processes have been developed for producing these materials.

It has been found that oil-modified alkyd resins behave according to the amount and nature of the oil present. This is defined generally by the expression "short oil length" or "long oil length." A short oil resin is one which contains less than 50 per cent of drying oil in its make-up. A long oil resin contains more than 50 per cent of oil in its make-up.

	% Glyptal	% Oil
Short Oil . .	60–70	30–40
Medium Oil .	50–60	40–50
Long Oil . .	33–50	50–66

The resins will behave according to the oil length. In the short oil resin the properties of the synthetic resin will predominate. Such resins are comparatively hard, and they are capable of being set by heating; coatings based on them are baked or stoved. Conversely, they will not be very soluble in oil solvents such as turpentine or white spirits. They may even be incapable of air drying.

Long oil resins will be much softer, more soluble in oils and solvents, less viscous, and capable of air drying. In other words, the properties are nearer to those of the drying oil. Generalising, the division of applications is that short oil resins go into quick-baking finishes such as are used for cars. Long oil resins are employed for making paints, inks, and air-drying finishes generally.

Apart from the drying oils, non-drying fatty acids or oils in amounts up to 40 per cent are also able to modify glyptals. They give resins which cannot be air dried. They are widely employed for modifyng nitro-cellulose lacquers with which they are compatible.

The behaviour of alkyd resins is therefore very dependent on the nature of the modifying oil. The actual ingredients combining with the alkyd resin are the fatty acid components of drying oils; thus, linseed oil or its component acids, tung oil or its components, etc., are the leading materials employed.

TABLE 157

COMPOSITION OF DRYING OILS

Linseed Oil consists of glycerides of

Linolinic acid	30%
Linoleic acid	49%
Oleic acid	5%
Saturated fatty acids (palmitic, stearic, etc.)	9%

Linolinic Acid.

$$CH_3—CH_2—CH=CH—CH_2—CH=CH.CH_2.OH(CH_2)_7.COOH.$$

Linoleic Acid.

$$CH_3(CH_2)_4CH=CH.CH_2CH=(CH_2)_7—COOH.$$

Oleic Acid.

$$CH_3(CH_2)_7CH=CH(CH_2)_7.COOH.$$

Tung Oil (China Wood Oil) consists of:

Glycerides of Eleostearic acid	80%
Oleic acid	14%
Stearic acid	6%

Eleostearic Acid.

$$CH_3.(CH_2)_3.CH=CH—CH=CH—CH=CH—(CH_2)_7—COOH.$$

It is, of course, well known that drying oils form hard skins when exposed to the air, owing to the catalytic influence of oxygen. However, if permitted to dry untreated, certain disadvantages are developed.

For example, raw tung oil gives wrinkled coatings; moisture resistance and strength characteristics are not very good. This behaviour is greatly improved if drying oils are submitted to a heating or bodying process. This is common practice in varnish manufacture. It is found that the iodine value increases, indicating that the unsaturation has become less, consequently a heat treatment is standard practice in the paint industry.

It is considered that the linear molecules which are present ordinarily become cross-linked during the bodying process so that a thicker, less soluble material is produced. It is found that when these drying oils are employed as constituents of alkyd resins it is essential that they should have the bodying treatment at some stage of resin production either before, during, or after resin formation.

Another characteristic feature of drying oils is that the drying or bodying process is rapidly accelerated by the presence of small quantities of metallic compounds. Driers such as linoleates, resinates, naphthanates of lead, manganese, cobalt, etc., are used. In a precisely similar manner driers perform a like function in the oil-modified alkyd resins.

The preparation of oil-modified alkyd resins has not proved easy, and much ingenuity has been shown. The necessity for high temperatures has been one great snag. One method of preparing oil-modified alkyd resin was developed by Walker and Hill.[11] The following example describes if:

37 parts Glycerol
74 parts Phthalic anhydride

with 50 parts of oleic acid and heated at 200° C. 10 parts of linseed oil are added, stirring and heated until the mixture is clear. Four further lots are added in a similar manner. The material is heated at 225° C. for 2½ hours. A hard, clear, flexible resin is obtained. Baird and Hill[2] first condensed a polybasic acid with excess of polyhydric alcohol. Consequently, there are free hydroxyl groups available: at least one-third of the original. This product is then reacted with a fatty oil and finally condensed with a polybasic acid to take up the hydroxyl groups.

Another process is to use a high boiling solvent to enable dispersion of the oil in the resin. Thus, Wright and Bartlett[14] dissolved glycerol, phthalic anhydride and tung oil in a solvent such as diethyl phthalate, which boils at 292° C. The reaction could be carried forward rapidly at high temperature. The final oil-soluble resin was precipitated out with benzene.

There has been great activity in preparing alkyd resins modified with rosin or other natural resins. Ellis[5] heated

50	Phthalic anhydride
33	Glycerol
75	Rosin

up to 250°C. A clear product was produced having acid number 68. A further 10 parts glycerol was added, temperature raised to 290°C. The final resin was transparent and had a low acid value. The reaction could be carried out with rosin esters. The resins obtained were completely compatible with nitro-cellulose.

Wicks[15] has recently given an excellent summary of alkyd resins.

Maleic Esters. In recent years resins have been made employing maleic anhydride instead of phthalic anhydride. Greatly improved resins have been obtained in this manner. In particular this type of resin is prepared with rosin as an ingredient.

The Germans produced maleic anhydride in an ingenious manner. Starting with tetrahydrofuran, this was oxidised by means of nitric acid to give succinic acid. Vaporised and passed over an aluminium catalyst at 300°C., succinic anhydride resulted. When chlorine is passed into this at 200°C., maleic anhydride distils off.

One of the leading developments for this work has been the use of maleic anhydride instead of phthalic anhydride. They have vastly improved properties. The outstanding characteristic is the rapid change to the infusible condition, leading to improvements in stoving coatings, etc. The compositions are affected both by heat or by oxygen, i.e. stoving or air drying finishes may be obtained.

Apart from these products, very useful derivatives are produced by modification of glyptal resins by suitable phenol-formaldehyde resins. Outstanding progress has been achieved in the use of glyptal resins to modify urea-formaldehyde resins.

Analysis of Alkyd Resins. The analysis of alkyd resins is rather a complex matter. Alkyd resins occur in conjunction with numerous other materials, such as oils, rosin, etc. They also occur together with cellulose esters, urea resins, and phenolic resins, and frequently plasticisers, such as dibutyl phthalate, may be present to modify one or other of the resins. It is, therefore, very necessary to remove other plastics and their plasticisers. These are generally removed by ether extraction, which leaves behind the alkyd resin.

The residue from ether extraction may then be tested for the presence of phthalate by the fluorescein test, or the phenol-phthalein test. The chief methods employed for examining alkyd resins are based on the work of Kavanagh.[7] The principles he employed were:

1. Acid can be added in proper amount to the saponified resin, to free all the fatty acids without liberating any phthalic acid.
2. The fatty acid can be removed by extraction with ether.
3. Phthalic acid can be freed by addition of more acid, and then removed by ether extraction.

Kavanagh's Method. Solids such as fillers, pigments, etc., are separated by means of a centrifuge. They are then reduced to ash, and subjected to ordinary analysis for metals.

The solid content of the resin is found by heating small quantities in open vessels at 150° C. for two hours. The treatment is continued until the weight becomes constant. If drying oils are present which may oxidise, the weight may begin to increase, which in any event is clearly indicated.

Acid Number, Oil and Phthalic Anhydride. The acid number, oil, and phthalic anhydride are determined on the same sample. It is convenient to report the results as percentage of glyceryl phthalate and oil in the solid resin, even though they may not exist as such in the resin.

Acid Number. The acid number is the number of milligrams of potassium hydroxide which must be added to 1 gram of resin to neutralise it to the phenol-phthalein end point.

Weigh 0·75 to 1·0 gram of resin (1 to 2 grams of resin solution) into each of two 250-c.c. Erlenmeyer flasks, add 25 c.c. of benzene and 25 c.c. of alcohol (95 per cent) and a few drops of phenolphthalein, and titrate with aqueous 0·1 N potassium hydroxide until the pink colour develops. If the acid number is greater than 15, the end point will be indefinite and the observed value for acid number low. In this case, determine the acid number on a separate sample dissolved in 50 c.c. of acetone. Naphthenate driers may increase the acid number several units.

Oil. To each flask, after the acid number determination, add 10 c.c. of aqueous 6 per cent potassium hydroxide solution to saponify the resin. Place an air condenser in the neck of the flask, and heat on a hot plate until the benzene is removed. Remove the air condenser, and boil until the solution foams. If any odour of hydrocarbons remains, add alcohol and boil down again. All the high-boiling hydrocarbons must be removed now, or the oil determinations will be high and erratic.

Dissolve the soap in 10 c.c. of water. Add several drops of methyl red solution and 10 per cent hydrochloric acid from a pipette until the cloud of fatty acids just begins to form. Add 10 to 20 c.c. of ether and a more dilute solution of hydrochloric acid until the aqueous phase turns faintly pink. More indicator may have to be added to the aqueous phase in order to give a perceptible colour. This is the most difficult and important part of the procedure: difficult, because the ether extracts the indicator from the aqueous phase; important, because all the fatty acids must be liberated without freeing any phthalic acid. Any other mono-basic acids (benzoic, rosin, etc.) which are present will be freed and will be extracted along with the fatty acids if soluble in ether.

If the resin contains phenolic resin, the phenols will be extracted by the ether and may interfere with the oil determination. Decant the ether into a 250-c.c. beaker, add 10 c.c. of ether to the contents of the flask, and transfer to a separatory funnel. Run off the aqueous solution into the flask and the ether into the beaker. Extract once or twice more. Boil off the ether from the beaker on an electric hot plate. When only a few drops of water remain, place the beaker in an oven at 55° to 60° C. for several hours until the fatty acids are dry. Dissolve the dry, fatty acids in 5 c.c. of ether, and filter through a 3-cm. filter paper into a 30-c.c. flask. Wash the fatty acids from the sides of the beaker with more ether, but keep the final volume of ether in the flask less than 20 c.c. Evaporate the ether without boiling. Place the flask in the oven at 55° to 60° C. for several hours; then weigh at half-hour intervals until the weight is constant. Dissolve the fatty acids in 50 c.c. of neutralised alcohol and titrate with aqueous 0·1 N potassium hydroxide to the phenolphthalein end point. Calculate the acid number of the fatty acids.

Duplicate titrations should agree within 5 units of acid number. If one is much lower than the other, the low one may have been heated too much after the ether was removed and some anhydride formed. The acid number will be lowered by rosin, fossil-resin acids, or phenols, and raised by benzoic acid.

From the amount of potassium hydroxide used, calculate the quantity which is added to the weight of the fatty acids to give the weight of the triglyceride. The weight of the triglyceride is called the weight of oil.

$$\text{Weight of fatty acid} + (0{\cdot}00127) \times (1 \text{ c.c. of } 0{\cdot}1 \text{ N KOH}) = \text{weight of oil.}$$

This calculation does not indicate that oil was put into the resin as such; it may have been all fatty acids.

A rosin test should be made on the extracted fatty acids rather than on the resin.

Fatty acids may be tested qualitatively for the presence of rosin by the Liebermann-Storch reaction. A few drops of the fatty acids are warmed in a test tube with two or three times the quantity of acetic anhydride. When cold a drop of this mixture is placed on a spot plate, and a drop of 50 per cent sulphuric acid on a glass rod is mixed in. The production of a reddish-violet coloration which rapidly fades indicates the presence of rosin.

Phthalic Anhydride. To the aqueous solution remaining in the flask after the fatty acids have been extracted, add several millilitres of concentrated hydrochloric acid. Extract the solution three times with 10-c.c. portions of ether, combine the ether extract in a 250-c.c. beaker, and evaporate the ether. A few drops of water will remain with the phthalic acid.

In the meanwhile, evaporate the aqueous solution until potassium chloride begins to crystallise out. Cool, add just enough water to dissolve the potassium chloride, and extract with ether three times as was done before. Add the ether extracts to the beaker which contain the phthalic acid, evaporate the ether, and place the beaker in a warm place (not over 50° C.) until the water and hydrochloric acid are removed.

Add 50 c.c. of water and a few drops of phenolphthalein solution to the beaker. Run in from a burette a slight excess of 0·1 N potassium hydroxide. Heat until all the phthalic acid has dissolved, and titrate the hot solution with 0·1 N hydrochloric acid until the pink colour barely disappears. The potassium hydroxide and hydrochloric acid solutions should be standardised with phthalic acid, phthalic anhydride, or potassium acid phthalate under the same conditions.

$$1 \text{ c.c. of } 0{\cdot}1 \text{ N KOH} = 0{\cdot}0074 \text{ gram of phthalic anhydride}$$
$$Fx \text{ phthalic anhydride} = \text{glyceryl phthalate}$$

If the acid number of the resin was below 10, or if the theoretical amount of glycerol or more was used in the manufacture of the resin, the factor $F = 1{\cdot}293$ can be used.

REFERENCES

1 Arsem. U.S.P. 1,098,776/1914.
2 Baird and Hill. B.P. 364,737/1932.
3 Bigelow. *British Plastics*, 1948, **20**, 481.
4 Callahan. U.S.P. 1,108,329–30.
5 Ellis. U.S.P. 1,722,566/1930. U.S.P. 2,063,540.
6 Friedberg. U.S.P. 1,119,592.
7 Kavanagh. *Ind. Eng. Chem.* (Anal.) 1936, **8**, 397.
8 Kienle. *Ind. Eng. Chem.*, 1933, **25**, 971.

9 Kienle and Schlinghman. *J.S.C.I.* 1936, **55**, 228T.
10 Smith. *J.S.C.I.*, 1901, **20**, 1075.
11 Walker and Hill. B.P. 318,003/1930.
12 Weisberg. U.S.P. 1,413,144/1922.
13 Weith. *Polymerization*, Reinhold Inc., 1938, p. 281.
14 Wright and Bartlett. B.P. 235,589/1926.
15 Wicks. *Interchemical Review*, 1947, **6**, 63.

CHAPTER XXVIII

CASEIN AND OTHER PROTEIN PLASTICS

CASEIN has in the past been one of the leading plastic materials. Up to ten years ago it ranked second only to nitro-cellulose in importance. Casein has been one of the few proteins to find wide industrial application. Although mainly derived from milk, more recently other materials containing casein have become important. The outstanding example is, of course, the soya bean. Because casein is ordinarily derived from milk, it is a material with which most people are familiar. More nonsense has been talked and written about it than almost any other material.

In 1931 world production of casein plastic was of the order of 10,000 tons per annum. In recent years its popularity has waned, although annual products of casein has actually grown, and is of the order of 80,000 tons per annum. This is due to the fact that it does not lend itself to rapid processing and finishing. Other materials giving equal performance can be produced by mass-production methods. However, great efforts are being made to find means for accelerating processing operations. Should such a method come about it is possible that there would be a notable revival in the use of this plastic, which has many attractive characteristics.

U.S. requirements are of the order of 80 million pounds per year. Her production is about 12 million pounds, while Argentine, the largest producer, has capacity of about 60 million pounds per year.

It has found its widest use in Europe. Apart from the production of buttons its use in the United States has been comparatively limited, partly owing to the long processing period and partly due to the fact that climatic conditions are not very suitable for the material. It is a fact that comparatively little is known about the fundamental characteristics of the material and its behaviour. The falling demand is in part due to this state of affairs.

The value of casein as a plastic is entirely dependent upon its reaction with formaldehyde. The effect of formaldehyde was discovered by Spitteler in 1897. The cause of his work on the subject was a competition in Germany, designed to prepare white blackboards for teaching purposes. These apparently were considered to have superior optical characteristics. It took a number of years to get the technical characteristics of casein and processing details worked out. Thereafter, large-scale production began in Germany and in France, making the material which was known as Galalith. A few years later materials were developed in this country known as Erinoid[4] and Lactoid,[7] which have had great popularity.

The Preparation of Casein. The casein used for plastics is made from skimmed milk. It is important not to have fats, sugars, etc., present, as these create technical difficulties. Separated milk in the normal way contains about 9 per cent of non-fatty solids. In Great Britain in the past the disposal of skimmed milk has been a matter of some difficulty.

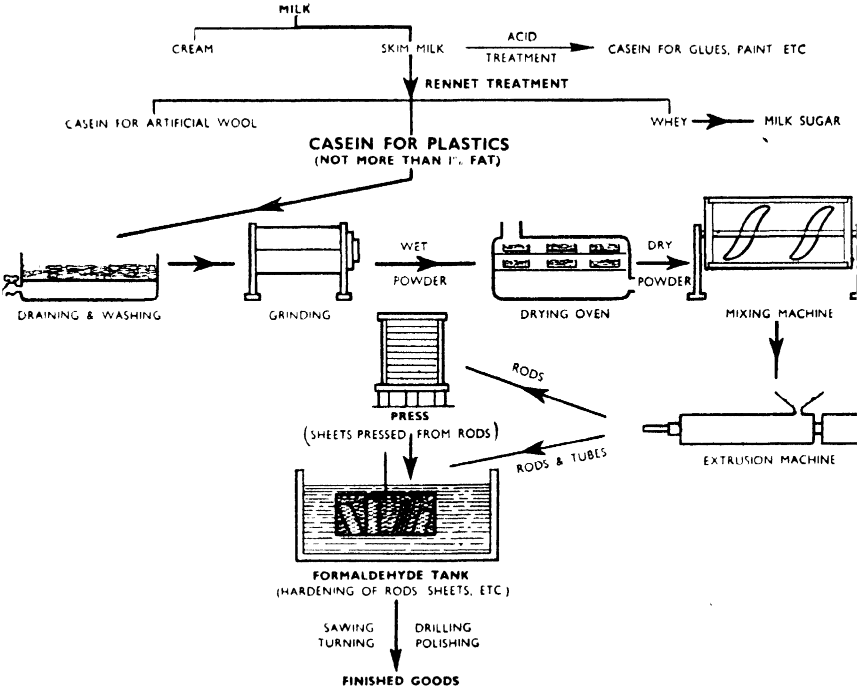


Fig. 238. Flow sheet for casein plastic

Rennet—an enzyme obtained from the stomachs of pigs—is added to slightly warmed skimmed milk. Within a quarter of an hour curds are formed. It has been found that casein prepared by other methods, for example, by means of acid coagulation gives a material which is unsuitable for plastics. On the other hand, acid-precipitated casein is excellent for glues and adhesives. The two types differ in their properties.

Casein is soluble in dilute solutions of alkaline materials such as sodium hydroxide, sodium carbonate, ammonia, borax, etc. It is soluble in acetic acid, formic acid, lactic acid. It will also go up in dilute solutions of acids. It is not soluble in water, alcohol, glycerine, and most solvents.

The curds formed in this way are broken up, the whey is drained off, and the curds washed. They are then subjected to hydraulic pressure to get rid of water. After passing through a grinding mill they are dried at about 40° C. The casein is then in a form suitable for conversion into a plastic material. It is essential that it should be kept to a definite moisture content not exceeding 11 per cent. By this procedure 1 lb. of casein is obtained from 3½ gallons of skimmed milk. Rennet casein has a fairly high proportion of calcium compounds present.

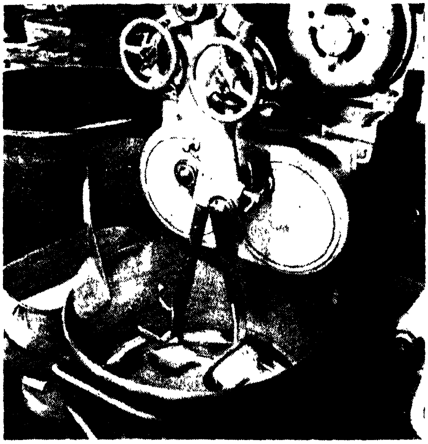


Fig. 239. Mixer used to prepare casein plastic

Preparation of Casein Plastic. Casein is insoluble in water. It does, however, swell in water to a considerable degree. This behaviour is utilised in the preparation of the plastic. A batch of casein is weighed out into a standard dough-mixing machine. The type known as an Artofex mixer is widely employed. Any dry pigments or any other ingredients are added at this stage. Dyestuffs are dissolved in a small quantity of water. Water is then added to give a dough of the desired consistency. Generally, about 40 per cent of water is required. Mixing is then carried out for a period of about fifteen minutes. It is found that casein has a marked affinity for acid dyes, an extremely useful feature. Other ingredients added include materials such as glycerine or methyl diphenylamine, which exert a plasticising action.

The chemistry of casein is still very obscure.[8] It is known to be made up of a combination of calcium caseinogenate and calcium phosphate. Rennin acts on the calcium caseinogenate with a strong gelling effect. The curds formed—calcium paracaseinate are modified under the action of formaldehyde.

Analysis of casein is not very helpful. A typical analysis has shown:

	%		%
Carbon	53·13	Nitrogen	15·78
Hydrogen	7·06	Phosphorous	0·86
Oxygen	22·4	Sulphur	0·77

According to Burk and Greenberg, the molecular weight of casein is 33,600.

Extrusion of Casein. Casein is mainly handled by extrusion. When a dough has been prepared as described above the material, which is still substantially in the form of a damp powder, is passed on to an extruder. The swelled casein, coloured by the dye which has been employed, is fed through a hopper on to the screw, which forces the material forward. The extruder is steam-heated, and under the influence of the heat and pressure the casein becomes fluid and plastic. It is finally forced through the heated die to emerge as a hot plastic mass shaped like the die.

Rods or tubes may be extruded in this manner, while if the final material is to be sheet, then the emerging mass may be forced through as a strip. The materials are cut to suitable lengths for handling.

Rods, tubes, or strips are immersed in water for a short time, and are then packed into crates, which have to be placed in cement-hardening tanks containing formaldehyde, for the so-called formolating process.

Mottled or streaked effects are produced by mixing small pieces of previously formed soft plastic having the desired colour or colours into the powder before it is extruded.

Production of Casein Sheet. Several methods are employed for preparing sheets of casein plastic. In one method extruded material is cut into suitable lengths, placed between metal plates in a hot press and squeezed down to sheets of the requisite thickness. These sheets are trimmed and then placed in crates for the finishing processes.

The alternative method for making casein sheet is to prepare a block of casein plastic. This is carried out by packing extruded material into a box-like press, and subjecting it to heat and pressure for some hours. In this manner a solid block of considerable thicknesses is prepared. This is attached to a planing machine, and sheets of any desired thicknesses are sliced from the block in the normal manner. They are then passed on for treatment with formaldehyde.

TABLE 158

GENERAL CHARACTERISTICS OF CASEIN PLASTICS, SHEET, ROD AND MOULDINGS[6]

Form	Colour	Ash %	Nature of mineral matter	Specific gravity at 20°C.	Water absorption (24 hr. at 20°C.) %	Loss on heating (6 hrs. at 110°C) %	Remarks
Moulding	Cream	8·8	Zinc oxide, some magnesium oxide & calcium phosphate	1·34	6·7	4·8	All normal alkaline case in mixtures, having 5 to 10% zinc oxide loading, and lake pigment or dyestuff.
Rod	Red	7·5	Aluminium lake, zinc oxide and calcium phosphate	1·33	5·0	3·2	
Rod	White	10·0	Aluminium lake, zinc oxide and calcium phosphate	1·36	5·1	3·2	
Rod	Blue	8·5	Aluminium lake, zinc oxide and calcium phosphate	1·35	5·1	3·0	
Rod	Green	8·5	Aluminium lake, zinc oxide and calcium phosphate	1·34	3·1	2·8	
Rod	Yellow	8·0	Aluminium lake, zinc oxide and calcium phosphate	1·34	4·0	2·8	
Sheet	Red	5·0	Aluminium lake, zinc oxide and calcium phosphate	1·33	8·5	12·0	
Sheet	White	12·0	Aluminium lake, zinc oxide and calcium phosphate	1·31	6·5	6·0	
Sheet	Blue	10·0	Aluminium lake, zinc oxide and calcium phosphate	1·36	6·5	5·5	
Sheet	Green	10·0	Aluminium lake, zinc oxide and calcium phosphate	1·34	7·0	7·5	
Sheet	Yellow	9·0	Aluminium lake, zinc oxide and calcium phosphate	1·33	6·8	7·2	

An unlimited range of different designs and colour effects can be obtained quite easily. Tortoise-shell sheets, for example, are produced by extruding thin rods of dark material, cutting them into short lengths. These are then mixed with a batch of powdered material, which would ordinarily give a transparent product. The entire mass is then extruded. By variations of this method a variety of streaked and mottled products can be obtained, rivalling horn in appearance and behaviour. Apart from this, metallic effects, mosaic, pearl-like products, jade, amber, and so on, are prepared without difficulty.

The Formolating Process. If any of these casein products are left after extrusion without further treatment, they rapidly lose moisture and become useless. To have any utility they must be immersed in a 5 per cent formaldehyde solution. The various products, stacked in suitable crates, are immersed in formaldehyde solution in concrete tanks. The time of immersion may vary from several days for thin products up to several months for thick sections. After the treatment sheets are suspended and allowed to season for a time. Inevitably there is warping and this must be corrected. Sheets are flattened by being pressed and then passed through abrasive rolls. Rods and tubes are straightened out while soft. They are then brought to the requisite dimensions by trapping. The process of trapping consists of subjecting the products to the action of a series of revolving abrasive wheels.

Fig. 240. Pressing casein sheets

The Properties of Typical Casein Plastic. The specific gravity of a casein plastic is 1·33. The material is non-inflammable, although it burns very slowly if held in an open flame. It burns with the distinct smell of burning feathers. It has fairly good electrical characteristics, and is employed to make articles which are to be used at low tension. The resistance to heat is quite low for casein tends to discolour about 70° C. and chars somewhat readily. The great disadvantage, however, is the extent of water absorption. For example, rods immersed in water at 70° C. take up 3 per cent in diameter in one day, and 10 per cent in 3 weeks. The increase in weight is about 5 per cent in one day and 25 per cent in 3 weeks. It is this poor water resistance together with the long processing, which are the outstanding drawbacks of casein.

Casein plastic strongly resembles natural horn in texture and appearance. It is fairly readily distinguished by heating with a little dilute sulphuric acid. Natural horn gives a peculiar odour, which is quite different from that produced by casein. It is odourless and tasteless.

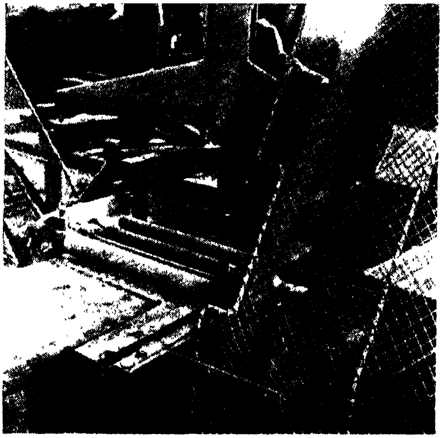


Fig. 241. Sanding casein sheets

If immersed in hot water at 100° C. it becomes thermoplastic and workable. When cooled rapidly it returns to its rigid condition. In this thermoplastic condition it can be blanked, and to a limited degree moulded.

TABLE 159

PHYSICAL AND CHEMICAL PROPERTIES OF LACTOID

Specific gravity	1·32–1·39
Tensile strength	4,500–10,000 lb. per sq. in.
Impact strength (Charpy)	25–45 cm. kgs. per sq. cm. (Test specimen 0·45 sq. cm. cross section)
Dielectric strength	216 (R.M.S.) volts per mil. (Test specimen 2 mm. in insulating oil at 15° C.)
Volume resistivity (polished)	11,000 megohms per cm. cube
(unpolished)	5,800 megohms per cm. cube (Test specimen at 16° C. and 51% relative humidity)
Surface resistivity (polished)	80,000 megohms
(unpolished)	32,000 megohms (Test specimen at 16° C. and 51% relative humidity)

From the point of view of fabrication it is an admirable material to handle. It can be sawn just like wood; it can be readily turned, drilled, punched, cut, and embossed. All these operations can be carried out with ordinary tools suitable for handling wood.

Casein is outstanding for the brilliancy and range of colours which are available and for the ease with which it can be polished to a remarkable lustre. Another interesting feature is the fact that the finished material can be readily dyed without great difficulty. A solution of an acid dye at 60° C. will effectively colour white casein to any required intensity.

The chief application of casein plastic has been in the button industry. In the past most buttons were made from the material. Other outstanding applications include knife handles, and handles generally, spectacle frames, brush backs, buckles, brooches, beads, chessmen, cigarette holders, jewellery, knitting needles, propelling pencils and fountain pens, umbrella handles, etc.

Preparation of Buttons and Buckles. A special technique has been developed for the preparation of buttons from casein. Rennet casein, water, and colouring material together with 2 per cent of alum are mixed and extruded. The effect of the alum is to make the plastic stiff enough to be handled on slicing machines. Extruded rod is sliced into disc shape blanks which are the button form. Being quite thin these are hardened in a few days in formaldehyde. They are then drilled in automatic machines. Very high drilling speeds can be used as the plastic shows no tendency to clog.

Buckles are made by extruding the plastic as ribbon and punching out the shape.

Polishing Casein Plastics. Casein plastics acquire outstanding polish by being immersed in a solution of warm sodium hypochlorite for a few minutes. The material is first subjected to buffing where necessary. It is then placed in a solution of 2 per cent sodium hypochlorite at 70° C. to which a little caustic sode has been added. After three minutes it is washed in warm water and rinsed. The surface is soft when the articles have been removed from the bath, but sets to a hard gloss when dry. When allowed to dry a brilliant polish has been acquired. It is claimed that this finish gives improved water resistance. In some cases the articles are finished off by being subjected to a tumbling process with wax and wooden pegs.

Recent Developments with Casein. Many efforts have been made to overcome the disadvantages of casein in order to shorten the time of hardening. Materials such as ammonium chloride or ammonium thiocyanide have been added to the powder. Another angle has been to replace formaldehyde by other hardening agents such as hexamethylenetetramine. The intention has been to enable the casein to flow under pressure and then permit the hardening agent to function. Brothers[2] has described the preparation of protein which has been prehardened, with formaldehyde, giving material which can be shaped under heat and pressure and come from the mould as a finished article. The protein is treated with formalin solution rendered alkaline, after which excess formaldehyde is washed out and the material dried. He found that acid casein gave better products than rennet casein. Using ethylene glycol as plasticiser, he found that water absorption of this material was less then that of ordinary casein plastic. This moulded acid-casein after 24 hours' immersion gave 15 per cent moisture take-up as compared with 25 per cent by the usual procedure.

Fig. 242. Typical rumbler used for small articles made in celluloid, or cellulose acetate, or casein, or cast resins[10]

Soya Bean Plastics. A great deal has been heard about the use of soya beans for the preparation of moulding powders. The Ford Motor Company has been particularly active in this work. Their value is attributed to the large proportion of protein, mainly casein, in soya bean meal. Soya bean meal is the residue after oil has been extracted. It is being extensively used as an addition to phenol formaldehyde resin together with a certain amount of wood flour. The characteristics of the materials formed make it quite clear that the soya bean makes definite contribution to the characteristics of the material.

Mechanical mixtures of formaldehyde-hardened soya bean meal and phenolic moulding compounds possess thermosetting characteristics.[3]

Such a mixture in a 50–50 proportion gives products which compare favourably with those obtained by the phenolic moulding compounds alone. They require the same curing time.

Formaldehyde-hardened soya bean meal in mixture with phenolic resins does not act as a filler in the same way as wood flour. It is more correct to consider the phenolic resin as a plasticiser and a modifier of the hardened protein plastic.

The replacement of wood flour in phenolic plastics by soya bean meal causes a rapid increase in flow while the addition of increasing amounts of soya bean meal to constant ratios of phenolic resin and wood flour results in a gradual decrease in flow. These two effects can be balanced against each other to produce plastics having either higher flow or lower percentage of resin or both. The curing time increases with increasing content of thermoplastic soya bean protein. This effect can be diminished in practice by longer periods of rolling the plastic before moulding, use of paraformaldehyde accelerator, or preheating the moulding powder. The water absorption of soya bean-modified plastics is held within practical limits by a preliminary leaching and heat denaturation of the meal and by preparing the plastics by the wet mix instead of the dry mix method. The flexural strength varies slightly, and the impact strength decreases with increasing content of soya bean meal; loss of impact strength is less for the wet method than for the dry method. Coloured soya bean-modified phenolics may be produced with organic dyes; they have a greater depth of colour and are more stable to light than standard phenolics.

Mixtures of 60 per cent formaldehyde-hardened soya bean meal and 40 per cent phenolic resins, compounded on heated mixing rolls, produce a good thermosetting moulding plastic, but one inclined to be somewhat resinous. The alkali commonly used to catalyse the cure of the phenolic resin appears to weaken the water resistance of the hardened protein.

Incorporation of 25 per cent wood flour with equal parts of formaldehyde-hardened soya bean meal and phenolic resin produces thermosetting plastics with as fine a finish, as great strength, as short a cure, as permanent as average phenolic plastics, and with greater possibilities for colour and shade production.

Protein Fibres. One of the outstanding activities with milk casein, soya bean casein, and other proteins, has been the preparation of fibres from them. Ferretti[5] in Italy was the pioneer in this development, his original material was known as "*lanital.*" Although at first there was a great deal of scepticism, the production of these fibres has assumed considerable volume in different parts of the world.

They have been produced in Italy, Germany, Holland, the United States, and to a small extent in this country. The principle involved is to disperse protein in an alkali solvent, extrude the solution through fine apertures into an acid bath. The fibres formed in this way require further treatment, generally with formaldehyde, in order to give them the requisite strength. According to Ferretti, casein which has been prepared by treatment of skimmed milk with sulphuric acid or lactic acid give the best fibres. Whittier and Gould,[9] the leading American exponents in this field have obtained satisfactory fibres with 8–12 per cent casein solutions, and suggest that the most practical type is the 10 per cent solution working at 50° C.

American production of one type, "*Aralac*," is of the order of some million pounds per year. It is used as a textile fibre and for felt hats. Price is about 64 cents per pound.

They have summarised the leading solvents for casein suitable for the purpose as sodium hydroxide, trisodium phosphate, ammonium hydroxide, triethanolamine, and sodium pentasulphide. In each case only a little more than the minimum necessary for solution is desirable. They found that small quantities of aluminium salts of barium greatly enhanced the strength and the flexibility of the fibres produced. They also found that additions of 1 per cent of oleic acid, linseed oil, turkey red oil, sodium tartrate, glycol phthalate, butyl tartrate, or urea, added flexibility to the fibres.

TABLE 160

FORMULA FOR SPINNING

Spinning Solution (in water) %		Precipitating Bath (in water) %	
Casein	10·0	Sulphuric acid	2·0
Oleic acid	1·0	Formaldehyde	5·0
Sodium hydroxide	0·27	Glucose	20·0
Sodium aluminate	0·87		

So far as the precipitating solution was concerned, they considered that 5–10 per cent solutions of sulphuric acid, phosphoric acid, acetic acid, etc., were effective. Dehydration of the fibres was greatly aided by the presence of 20 per cent glucose.

It was necessary to treat the casein fibre to enhance the strength, and 5 per cent formaldehyde has been the outstanding material employed, although other aldehydes have also been used. The following was a typical procedure carried through by Whittier and Gould:

"The casein is allowed to swell for half an hour in about half of the required quantity of water used for the spinning solution, and the sodium hydroxide is added as an 8 per cent solution. The solution is then stirred until it is uniform, the oleic acid added, the solution stirred again, and the sodium aluminate added in the form of a solution in the rest of the water. The solution is again stirred thoroughly and then deaerated by keeping it under vacuum for several hours. It is then ready to spin.

After the two solutions are brought to the same temperature, for example 50°C.—the spinning solution is extruded under pressure through a rayon spinneret into the precipitating bath and wound on a bobbin. The fibre is immersed in a 5 per cent formaldehyde solution for 16 hours, then in a 5 per cent oil emulsion and dried."

Boyer[1] has described the methods used by the Ford Motor Company to make fibres from soya bean proteins. They prepared 20 per cent solution of protein which required to be ripened before it could be used. The solution was forced through spinnerets into a precipitating bath which consisted of sulphuric acid, formaldehyde, and a salt such as aluminium sulphide. The latter was intended to aid dehydration of the filament. The fibres were stretched during this procedure, a process which was considered to be of some importance. X-ray study of the fibres show that the stretching caused orientation in the fibres.

The fibres obtained by this method were white, soft, and had high resilience. Its strength was 80 per cent that of wool. It had an elongation of 40 per cent when dry, and 60 per cent when wet. The tensile strength being the same in both cases. The specific gravity was 1·31. The material was not wetted so readily as either casein fibre or wool.

Analytical Considerations. Casein plastics are generally easily recognisable. They may be confused with urea-formaldehyde plastics owing to the brilliant pastel shades available. Their softening behaviour in warm water and their reaction to acids and alkalis are sufficient to distinguish them.

Almost the only quantitative estimation is the nitrogen content. This is carried out by the Kjeldahl method. The actual casein content is found by multiplying the result by the factor for protein 6·25.

Casein and Horn. Casein plastics very closely resemble horn in many characteristics. It is as well to know how to differentiate between them. Hardened casein is partially soluble in 1 per cent potassium carbonate solution as well as in 1 per cent ammonium oxalate solution. Horn only dissolves to a very slight extent in the former and not at all in the latter. A product soluble in hot, dilute alcohol and separating from the cooled filtrate is obtained on treating hardened casein with iodine. Caustic potash dissolves the precipitate, which is again precipitated by acids. Boiling with ammonium chloride solution partially dissolves hardened casein. Boiling solutions of ammonium sulphate exert a similar but less pronounced action. Horn does not dissolve at all under these conditions.

REFERENCES

1 BOYER. *Ind. Eng. Chem.*, 1940, **31**, 1549.
2 BROTHERS. *Ind. Eng. Chem.*, 1940, **31**, 31.
3 BURLISON. *Ind. Eng. Chem.*, 1936, **28**, 774.
4 *Erinoid.* Trade Mark of Erinoid Co., Ltd.
5 FERRETTI. B.P. 483,731/1938; B.P. 483,807/1938.
6 HALLS. *Plastics*, 1941, **5**, 123.
7 *Lactoid.* Technical Data of B.X. Plastics, Ltd.
8 SUTERMEISTER. *Casein and Its Industrial Applications*, Reinholds Corp. N.Y., 1939.
9 WHITTIER AND GOULD. *Ind. Eng. Chem.*, 1940, **32**, 906.
10 Photographs by courtesy of B.X. Plastics, Ltd.

CHAPTER XXIX

SILICONE PLASTICS

In recent years a new class of semi-inorganic high polymers, based on silicon instead of carbon, has become commercially available to the plastics and allied industries. They have been hailed as panaceas for many industrial activities. Bridging the gap between completely organic and inorganic products, these new materials are finding widespread application in the form of liquid dielectrics, lubricants, greases, rubbers, varnishes, and resins. They impart to the compounds in which they are used a broader range of service temperatures, good dielectric properties, and general inertness. They may be either thermosetting or thermoplastic.

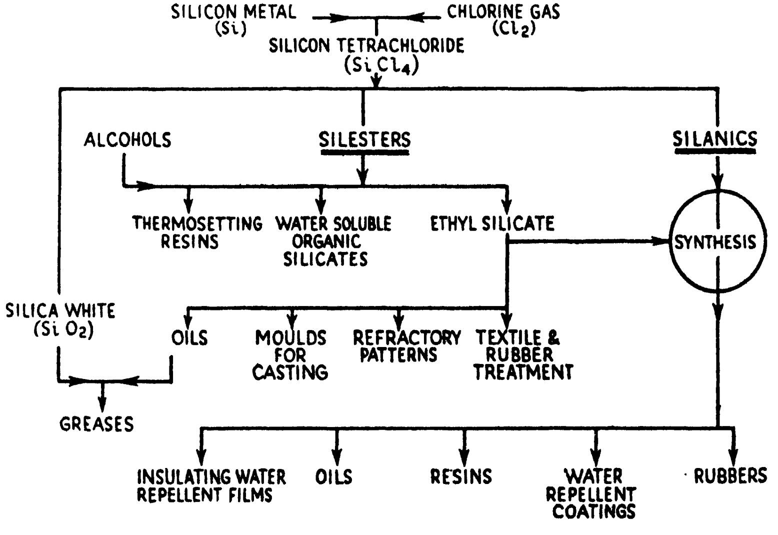


Fig. 243. Organic Compounds of Silicon

The pioneer work leading up to the formation of silicones was carried out by Kipping in Great Britain. Kipping[5] found in 1904 that organic radicals could be attached to silicon by means of the Grignard reagents.

The silicones are largely the results of the work of glass technicians who are primarily concerned with silicon compounds. Where plastics are made primarily of carbon atoms, glass chemists decided that silicon, being chemically analogous to carbon, might also yield plastics. As glass is a silicon compound, a study of its make-up could provide enough information to create new plastics materials of industry retaining certain desirable properties of glass and some newer ones of the resins.

These silicone high polymer products are made from sand, brine, coal, and oil. From a chemical viewpoint these resins are an important departure, differing from conventional plastics, in as much as carbon is replaced by silicon. Next to oxygen, silicon is the most abundant element on earth, usually found in the combination with oxygen as silica. The name silicones covers organo-silicon oxides, polymers, and cross-linked polymers. The kinds and structures of these resins may be varied according to the number and kind of radicals attached to the basic silicon atom. Thus, it is possible to create ethyl, methyl, and methylphenyl silicones. Silicone molecules are large and infinitely variable and can be specially designed in their properties for specific uses.

Formation of Silicones. As in the case of organic plastics from coal, air, and water, the synthesis of silicone resins involves considerable processing.

Although the basic elements of silicones are silicon and oxygen, the two most abundant elements in the earth's crust, the silicon atoms must also carry one or more hydrocarbon groups joined to the silicon through carbon. This provides solubility of the intermediate condensation products in organic solvents and promotes flexibility in the more or less completely condensed resins.

The first stage is the replacement of one or more chlorine atoms attached to silicon by organic radicals through the use of magnesium metal in the form of Grignard reagent. This reaction, discovered by Kipping in 1904, allows wide choice of groups and permits considerable versatility in planning the properties of silicones for specific uses. The organo-silicon chlorides are then treated with water to replace the remaining chlorine atoms with hydroxyl groups. Condensation of the hydroxy organo-silanes, or silanols, follows to build up high polymeric units except in the case of the tri-substituted silanol, which can condense only once to form a disiloxane, the silicon analogue of simple ethers.

The silanols may be said to be the "monomers", although they usually condense as fast as formed under the conditions of hydrolysis. Silanediols, having two of the four valences of the silicon atom blocked with organic groups, can condense in only two directions. Silanetriols, having only one valency occupied by an inert group, can build up polymers in three dimensions. Hydrolysis and condensation of the variously substituted chloro-silanes can thus give rise to an infinite variety of high polymeric products, varying from liquids through thermoplastic solids to glass-like resins.

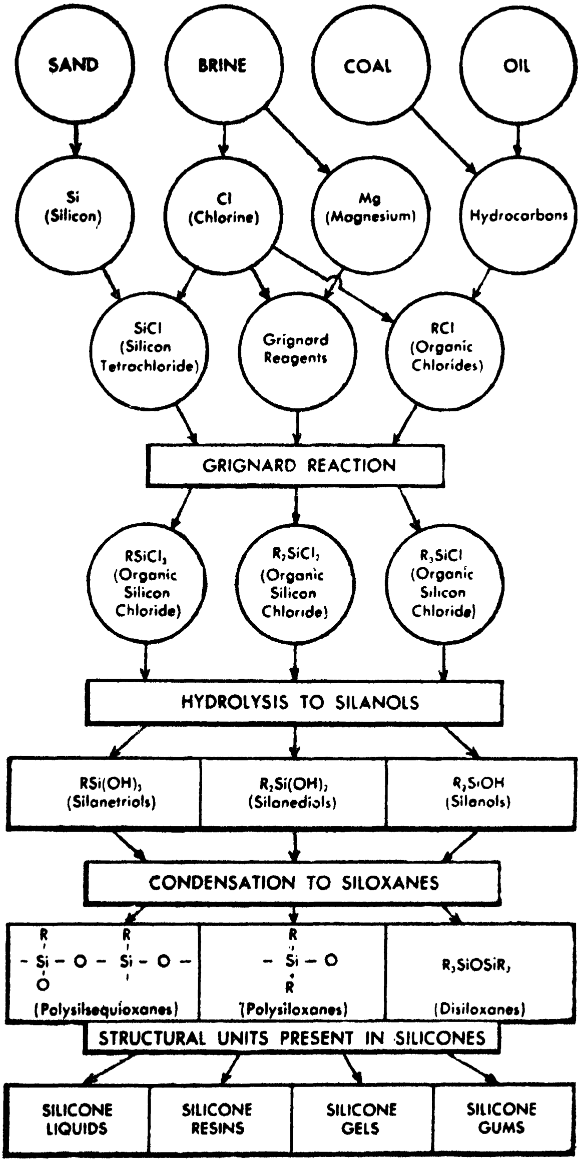


Fig. 244. Derivation of Silicone Plastics

The following example is typical of the reactions which may be used to make silicones in the laboratory:

1·65 mols of p-dibromobenzene in ether solution are caused to react with 3·45 mols magnesium. The resultant phenylene-di-magnesium bromide is added with stirring to an ether solution of silicon tetrachloride and the mixture is heated under reflux for 30 minutes. The so-formed phenylene silicon dichloride is then added with stirring to 1·32 mols of the di-magnesium derivative of mixed isomeric dichlorpentanes in ether solution and heated under reflux for two hours. The solution of organo-silicon complex is isolated by pouring into water, thereby dissolving out the magnesium salts. Evaporation of most of the ether yields an extremely viscous benzene soluble resin. Complete evaporation yields a solid, clear yellow resin with a non-tacky surface. Rochow[6] discovered that certain hydrocarbon chlorides react directly with silicon to form organo-silicon chlorides.

Most of the work on silicone resins has been carried out by the General Electric Company of America and the Dow-Corning Corporation. These companies are also the leading manufacturers at the present time.

Types of Resins Available. The first type of resin is in the liquid form. These may have a great variety of viscosities, boiling points, specific gravities, etc., all the other properties varying accordingly. They are permanently fusible, and may be treated as an ordinary non-volatile liquid.

The grease type is available in many different forms and is also permanently fusible.

The third type available is that in the form of a varnish. This is thermosetting, and may be baked to a hard film. It may be regarded just like any other type of varnish. The silicones (of the binder type) have already been used to bind mica and various other veneers together.

The next type is the moulding powder. It is not available commercially yet. It has been produced on an experimental scale.

The silicones are also available in a rubbery form. The type made by the Dow Chemical Company is known as Silastic. This is available in any consistency, hard or soft. Some can be vulcanised, but others are thermoplastic.

It should be remembered that any of the above types may be modified to a great extent, and the possible variations are almost infinite. A great variety of properties are possible.

Liquid Silicones. The series of water-white, odourless, inert liquid silicones was among the early discoveries.[3] These are in commercial production. Most of them are simple ethers. These liquid silicones have the following properties:

1. Water-white, brilliantly clear, mobile liquids which remain fluid at arctic temperatures.
2. Stable to heat, neutral in reaction, chemically inert and non-corrosive to metals.
3. Unusually low rate of viscosity change over a wide temperature range.

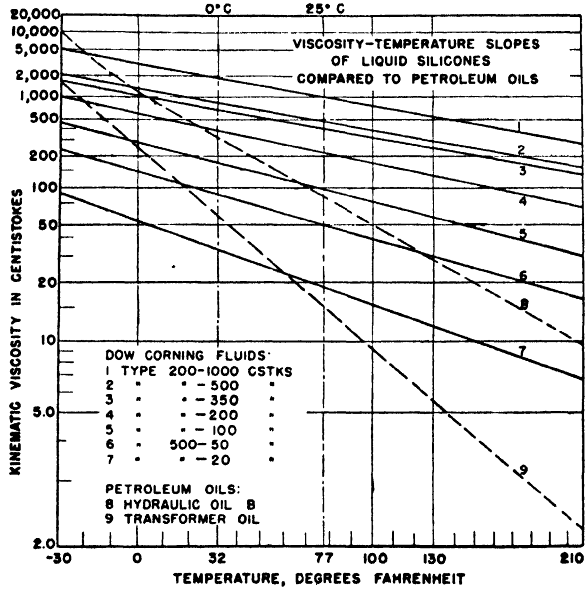


Fig. 245. Viscosity of Silicone Fluids[1]

4. Higher flash-points than petroleum oils of equivalent viscosity.
5. Low surface tension (20 dynes/cm.). Readily wet clean, dry surfaces of glass, ceramics, and metals.
6. Highly resistant to oxygen, oxidising agents, mineral acids, and corrosive salt solutions.
7. Incompatible with synthetic rubber polymers and the polymers used in organic plastics.
8. Insoluble in water and the lower primary aliphatic alcohols; soluble in most organic solvents.
9. Non-volatile, except for low viscosity grades. Weight loss and vapour pressure negligible up to 400° F.
10. Low dielectric constant and power factor over a wide frequency range.

Uses. The silicone liquids are useful wherever there is a need for a liquid with a low rate of change of viscosity with temperature where retention of fluidity at low temperatures is required, or non-volatility at elevated temperatures. These properties, together with inertness towards metals, coatings, and gasket materials, make silicone fluids of outstanding importance for use as damping fluids, gauge fluids, etc. Because of their exceptional resistance to chemicals, they have also proved useful as impregnants for asbestos packings and gaskets in chemical pumps.

Silicone liquids do not exert any solvent action on high polymeric materials used in plastics even at elevated temperatures. For this reason, they are useful mould release agents, particularly in the injection moulding of hollow articles. When so used, they produce a water-repellant surface on the moulded plastic which has greatly increased surface resistivity.

The silicone fluids have good electrical properties. All the silicones, both liquid and solid, share these good electrical properties. Outstanding features are the low dielectric constant and low power factor over a wide frequency range.[2]

Delectric constants vary between 2·7 and 2·8 at 20° C. and are fairly constant at all frequencies. Power factor is about 0·0001 at 1,000 cycles and varies little at very high frequencies.

Grease-type Silicones. The grease type of silicone may be regarded as a development of the liquid type. The properties of the silicone greases may be regarded in general as being very similar to those of high viscosity liquid silicones. The grease remains as a grease even at high temperatures, in strong contrast to petroleum products which melt. They are available in a wide range of consistencies. Generally, they are translucent, having the consistency of petroleum jelly. These greases may be used satisfactorily even at 200° C., or possibly more. They also maintain their consistency to a lower limit of about —40° C.

Properties of the Varnish Type. The previous two grades of silicones have been thermoplastic. It is possible to obtain thermosetting types, and the valuable applications to which they lend themselves are dependent on this property. The materials are derived from specially prepared resins, which are capable of growing in three dimensions, as in the case of other thermosetting plastics.

The primary advantage of the varnish-type silicone resin is great thermal stability and resistance to moisture.

It will readily withstand tough service conditions, can readily be used as an impregnant and adhesive, and may be applied in the same way as any conventional organic varnish. It is resistant to oils, chemicals, and the like. The excellent electrical properties of the silicones are evident from the applications. The silicone varnishes have good track resistance, and the electrical properties are maintained at high frequencies. Increased temperatures do not greatly affect the values. In the case of the liquid silicones, although the power factor does increase with temperature, it remains lower than that of a typical transformer oil.

In applying the resins, they should be baked to a tack-free surface. This may usually be accomplished by giving a cure equivalent to 2 hours at 250° C., or, if not convenient, about 2 to 4 hours at 150° C., followed by 2 hours at 200° C.

These varnishes are already used as impregnants. The ease with which they wet surfaces is quite outstanding.

Electrical equipment can be designed and built to withstand high temperatures by using inorganic spacing materials, such as glass fibres, asbestos, and mica. However, such machines require temperature-stable resinous dielectrics to fill in voids, hold the conductors in place, insure good heat conductivity, and keep out moisture. Many impregnating resins and varnishes will exclude water as long as they are not subjected to excessive thermal conditions. Due to the inherent stability of conventional organic insulating materials to heat, they eventually undergo thermal breakdown and become cracked or carbonised, thereby admitting water and conducting materials.

Silicone resins provide the heat-stable resinous dielectrics which are required in the following insulation constructions:

1. As an impregnant, coating, and binder for glass fibre served magnet wire.
2. As a varnish for impregnating and coating glass fibre or asbestos cloth, tape, and sleeving.
3. As an adhesive for bonding mica laminations to glass fibres or to asbestos cloth for use as ground insulation.
4. As an impregnating and sealing varnish for filling remaining voids and for completely waterproofing the assembled machine.

Glass fibre served magnet wire is impregnated with silicone resin and cured in conventional wire enamelling towers. The silicone resin fills the voids between the glass fibre yarns and permits the production of a smooth continuous insulation which is heat-stable and waterproof.

Silicone varnished glass-fibre cloth provides a backing to which mica films can be laminated by silicones as adhesives to produce ground insulation for lining the slot cell. Heat-resistant coil separators and slot sticks can be made of silicone varnished glass-fibre cloth laminated with silicone adhesives. After assembly, the remaining voids are filled by impregnating the equipment and baking it to cure the silicone resin impregnant. Baking conditions equivalent to about 2 hours at 250° C. are usually required.

Designers of electrical equipment have welcomed the new high-temperature silicon insulation because its improved thermal endurance can be utilised in three important ways:

1. To reduce size and weight of electrical equipment, without reduction in serving life, where operating temperature can be increased. A 50 per cent reduction in weight of electrical equipment has been found possible.
2. To increase greatly the serving life of insulation when it is necessary or desirable to maintain conventional size, weight, and operating temperatures.
3. To permit operation in ambient temperatures and humidities materially higher than those permissible for usual types of insulation.

One of the biggest applications is in connection with electric motors, where the efficiency has been increased. Inorganic insulation has been available for some time, but there have only been organic adhesives and impregnants available, which have not allowed the full value of the inorganic insulants to be brought out. For instance, magnet wire wound with glass can only operate at about 120° C. with ordinary insulants. This temperature may be increased to between 150° and 220° C., when silicone resins are used. So far as electric motors are concerned, this increase in operating temperature is general. The ambient temperature of operation may be increased enormously, moreover, under very humid conditions. It is possible for an electric motor, insulated with silicone resins, to operate continually up to about 200° C., and for short periods up to 300° C.

Moulding Silicone Plastics. Moulding powders are not yet commercially available because they are very slow curing, needing high temperatures for fairly long periods. They are far too costly at the present time.

Silicone Synthetic Rubber. A new elastomer based on silicones offers the possibility of some very unusual applications. The outstanding features of the silicone rubbers is the exceptionally wide temperature range through which they retain rubbery properties. The elastic properties are maintained at temperatures (for short periods) up to 200° C., and as low as —40° C. Continuous operating temperature is about 150° C. The top continuous operating temperature of natural and synthetic rubbers is about 80° C.

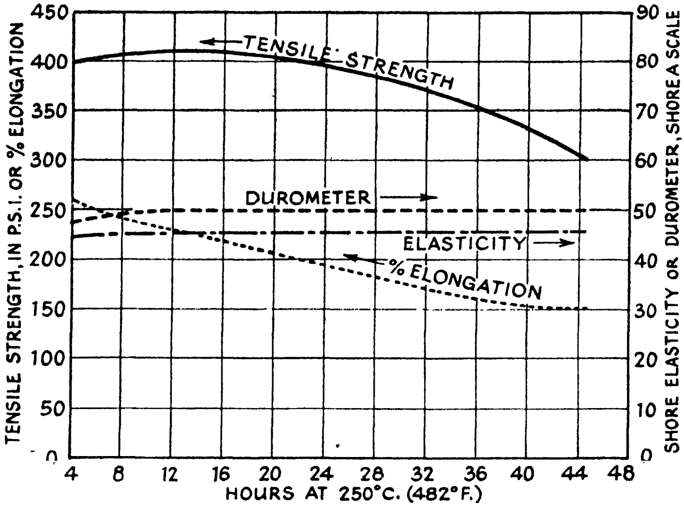


Fig. 246. Effect of Heat Ageing at 250° C. on Properties of Silastic 150[4]

Other ageing properties are superior to those of natural rubber. Ozone, corona effects and ultra-violet light have little effect on silicone rubbers, but are fatal to natural rubber articles.

The disadvantages of silicone rubber are the very poor tensile strengths and low resistance to tear.

TABLE 161

PHYSICAL PROPERTIES

Silastic stocks, cured for 48 hours at 390° F.	150	160	167	180
Density, at 25° C.	1·9	2·1	2·0	1·6
Hardness, Shore A Scale	45–55	55–65	55–65	75–85
Tensile strength, lb. per sq. in.	400	600	600	700
Elongation, per cent	300	200	110	75
Elasticity, Shore	30	40	40	15
Per cent impact resilience (Bashore Resiliometer)	53	52	54	47
Flex, de Mattia, Method B, per cent of elongation	70	50	20	20
Number of cycles	250,000	150,000	80,000	7,000
Per cent water absorption	2·58	0·88	1·26	0·45
Water absorption, mgm. per sq. in.	47	17	25	7

Also of importance is the lack of unsaturation, and therefore curing possibilities. This does not matter in some instances, but in others it is possible to incorporate double bonds into the formula, and some curing properties are conferred. The rubber may be mixed with the usual fillers and milled, extruded, etc., exactly like natural rubber. It is not compatible with natural or synthetic rubbers.

TABLE 162

ELECTRICAL PROPERTIES

Silastic stocks (cured for 48 hrs. at 390° F.)	140	160	167	180
Dielectric constant, at 10 cycles . .	5·6	9·0	9·8	4·6
Power factor, per cent at 10 cycles .	1·3	0·8	0·4	0·6
Power factor, per cent at 10 cycles .	1·0	2·0	0·1	0·3
Dielectric strength, volts per mil. .	500	500	500	650

One field of application is where shock absorption is wanted at high temperature. The recovery after being under compression at high temperature for long periods is almost perfect.

Plastic Elastic Silicones. Bouncing Putty. A by-product of the manufacture of the silicone elastomer is a peculiar substance, which feels like putty and may be deformed in exactly the same way, and yet, when dropped on to the floor, bounces like rubber. This effect of dilatency is very striking.

REFERENCES

1 BASS. *Chem. and Ind.*, 1947, **33**, 171.
2 BASS AND KAUPPI. *Proc. Inst. Radio Eng.*, 1945, **33**, 444.
3 Dow-Corning Fluids. B.P.572, 331.
4 Dow-Corning. Technical Literature.
5 KIPPING. J.C.S., 1904, **20**, 15; 1937, **159A**, 139.
6 ROCHOW. J.A.C.S., 1945, **67**, 963.

PART VI

SOME IMPORTANT ASPECTS OF PLASTICS

CHAPTER XXX

HIGH-FREQUENCY HEATING FOR PLASTICS: AN EXPLANATION OF ITS PRINCIPLES AND USES

HIGH-FREQUENCY heating of plastics has acquired great importance for various applications. It seems likely to have a most profound influence on plastics development. As knowledge of the method grows its value becomes more significant. It affords a means of eliminating the difficult factor of heat transfer in many materials. In many processes ordinary heating methods cannot effect rapid temperature rise in the products. The problem of uniform distribution of heat throughout a material has been a serious obstacle in plastics technology.

The new technique is being applied to moulding of thermosetting plastics, to laminating processes, and to welding operations with thermoplastics. The scope widens continually as knowledge of the technique spreads. Almost every electrical firm of repute has produced a range of high-frequency heating units for plastics manufacture.

Advantages. The outstanding advantages of the process are:

(*a*) It can rapidly and uniformly heat non-metallic materials.
(*b*) Very accurate control of temperature is possible.
(*c*) Accurate control of rate temperature rise is possible.
(*d*) All heat is in the material, so that immediately heating is stopped there can be no further temperature rise due to surrounding materials, etc.

The practical evolution of the method is largely due to the work of Leduc,[5] mainly directed at the vulcanisation and treatment of rubber.

Principles. According to Leduc, the principles involved are:

(*a*) When a homogeneous dielectric is placed in a uniform field of high frequency, the material becomes uniformly hot through the mass.
(*b*) The rise of temperature of the mass increases with the frequency and with the intensity of the field.
(*c*) The power absorbed increases with the electrical heterogeneity of the plastics compound. Addition of small amounts of materials of high S.I.C. have a profound influence.

How the High-Frequency Field Works. It is interesting to consider how a high-frequency electrical field causes heat production. In effect, the plastics is acting as the dielectric of a condenser. The electrical energy is stored in the dielectric, i.e. in the plastics. It is uniformly distributed throughout the material, no matter how thick it may be.

At least part of the energy distorts the molecules of the dielectric. When a condenser is discharged, the molecules tend to return to their original shape. In doing so there is rapid movement of the molecules. Friction effects are set up owing to resistance to the change, and as a result heat is developed. When the electrical field is rapidly alternating (i.e. charging and discharging the condenser, i.e. the plastic) in opposite direction a great deal of the energy is converted into heat throughout the material by hysteresis. In effect, therefore, the more rapid the change, i.e. the higher the frequency, the higher the heat production. The only other factor involved is that the material being treated should not have very low power factor at the frequency being used, which in effect means that the amount of electrical energy lost as heat must be a reasonable proportion. Thus it would be futile to use the method for polystyrene or polythene, which have very small power losses. The energy required for a particular heating operation, and the rate at which it must be applied, can readily be calculated. No question of ordinary heat transfer requirements is involved.

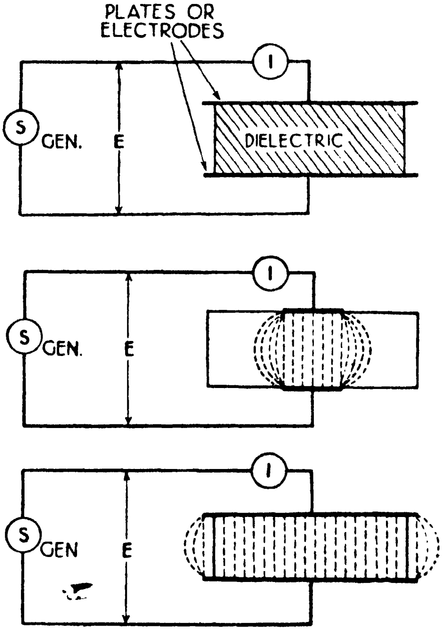


Fig. 247. Illustrating distribution of current as function of relative size of electrodes and dielectric

The power expended in heating the dielectric of a condenser depends upon the voltage, the frequency, the capacity and the power factor of the dielectric material, or

$$W = E^2 \times 2n \times \pi \times C \times P.F.$$

Where W is the energy dissipated in watts as heat in the dielectric, E is the voltage across the electrodes, n is the frequency, C is the capacity of the condenser formed by the material being heated, and P.F. is the power factor of the material. It is clear that since the capacity C and the power factor P.F. are constants for any given material heated and any particular set-up of the equipment, the energy input can be controlled by altering either the voltage or the frequency.

TABLE 163

POWER FACTOR OF PLASTIC MOULDING MATERIALS

	Megacycles			
	1	10	25	50
P-F. wood flour . . .	·130	·150	·161	·160
P-F. asbestos	—	·351	·244	—
U-F. cellulose	·035	·123	·144	—
Melamine (filled) . . .	·04	—	—	—
Cellulose acetate (filled) . .	·04–·06	—	—	—
Cellulose acetate . . .	·07–·01	—	—	—
Cellulose nitrate . . .	·1	—	—	—
Polyvinyl chloride . . .	·15	—	—	—
Polyvinyl chloride-acetate . .	·018	—	—	·018
Polyvinyl chloride-acetate (filled) .	·01	—	—	—
Polyvinyl butyral . . .	·06	—	—	—
Methyl methacrylate . . .	·025	—	—	·022
Nylon	·025	—	—	—
The following are not suitable for H.F. Heating				
Ethyl cellulose	·005	·006	—	—
Polythene	·0003	·0003	·0003	·0003
Polyisobutylene	·0005	—	—	—
Polystyrene	·0001	·0001	·0001	·0001

It is, therefore, practicable to use relatively low voltages. This ensures greater safety to personnel. The use of high frequency still causes high heat. It also avoids the danger of electrical breakdown in the material. It is quite possible to have a set-up where the material being subjected to the high frequency field may be too thin and will break down if the higher voltage is in use. For example, the heat obtained with 100 volts and 10,000,000 cycles (or 10 megacycles) per second frequency is the same as with 10,000 volts and 100,000 cycles. Within the normal range of frequencies used, the overall efficiency of the equipment remains substantially constant.

Electrical properties of the material being handled, such as capacity and power factor are only required as a guide to the setting up of the high frequency unit. Comparatively simple calculations give the power required and the time.

It is clear that the method offers a means of heating materials where uniform and rapid temperature rise is necessary, particularly where ordinary methods are difficult. High-frequency heating offers little advantage where ordinarily the use of external heat offers no difficulties. The efficiency of the method is lower than direct electrical heaters or steam heating, etc.

TABLE 164 EFFICIENCY POWER/HEAT

H.F.	50%
Electrical resistance heating . . .	100%
Fuel heating	70–50%

However, ordinary heating methods are not really satisfactory where heat must penetrate more than 0·5 inches. Consequently the method has a number of outstanding advantages which may be summarised as:

(*a*) It can rapidly and uniformly heat non-metallic materials.
(*b*) Very accurate control of temperature is possible.
(*c*) Accurate control of rate of temperature rise is possible.
(*d*) All heat is in the material so that immediately heating is stopped there can be no further temperature rise due to surrounding materials, etc.

The method has already found a number of applications in plastics technique. The outstanding applications are in the manufacture of resin-bonded wood and the preheating of moulding powders.

Laminated Wood. At present the process is being used chiefly in the manufacture of resin-bonded wood, a case where poor thermal conductivity of the material causes manufacturing difficulties. It can be said that applications of synthetic resins to the wood industry are being greatly increased by the use of high-frequency heating methods. Thus in extreme cases the time required to set a synthetic resin glue joint, often as much as six hours, has been reduced to minutes. The method has also been very successfully applied to the rapid drying out of green wood.

Ordinarily, in making laminated plywood, etc., in heated presses, it is very difficult to make large thicknesses, because a long time is required for the heat to get through to the centre. Long time of cure is required, outer layers tend to be over-cured while inner layers tend to be under-cured. In making laminated wood products, the high voltage terminal of the high-frequency output transformer is connected to a sheet of metal, so serving as one electrode, the sheet being sandwiched into a pile of glue-coated veneer sheets at a point midway up the pile. The other terminal of the transformer is then connected to the frame of the laminating press, so that both upper and lower platens become electrodes. These two outer electrodes are earthed, i.e. the press is earthed to assure the safety of operatives. Many layers of veneer, up to a total thickness of 2 feet or more, can be heated simultaneously, either to produce two single heavy slabs or for making a large number of thinner panels of laminate.

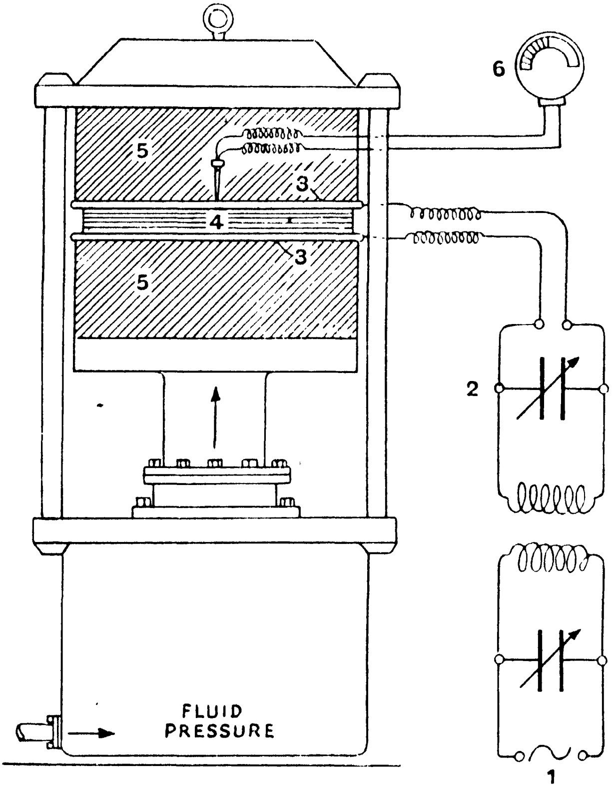


Fig. 248. Diagram of arrangement for the thermal treatment of resinoids in a high-frequency electrical field. Key: In the press is a five-plywood laminate bonded with a synthetic resin film. 1—the primary oscillatory circuit actuated by a suitable generator; 2—intermediate circuit; 3—aluminium condenser plates; 4—five-plywood undergoing HF treatment; 5—supporting wood blocks; 6—thermocouple needle indicator[9]

The method is effective in a few minutes, as compared with hours required for great thicknesses by conventional heating. The rate of production is enormously increased, while the quality of the products is also substantially improved.

Not only ordinary plywood, but also resin-impregnated compressed wood, can be made in this fashion. It is also possible to laminate heavy planks for keels, beams and girders, or, by omitting several veneer plies over a part of the area of the slab, to form a slab of varying density and strength, suitable for certain kinds of beams and for aeroplane propellers.

The method is applicable to laminated materials generally, whether the bonding agent is a phenolic resin, a urea resin, or a thermoplastic material. Similarly, the layers may be of wood, fabric, glass, etc.

In addition to the production of flat objects, it is also possible to form compound-curved laminated objects, such as wing and fuselage parts for aeroplanes. The electrodes need not be of heavy metal. Thin sheets of any conducting material can be used, for example, metal foil glued on to a wooden mould, or a mould or form of any material sprayed with metal.

Shape and design of electrodes require careful study. It is desirable to keep dimensions of the electrode small in relation to the wave length of the current flowing in it. Godfrey and Bilhuber state that with a frequency of two megacycles of 150 metres wave length the electrode size can be up to 25 metres in length.

Developments with synthetic glues have enabled the use of high frequency heating in complex wooden structures. The urea glues, while under pressure, will set at room temperatures in several hours. Most phenolic glues require heat to polymerise completely. Considering temperature limits in the use of the urea glues, it has been found that by raising the temperature to 75° C. the time required to create an effective glue joint can be reduced to two minutes. Increasing the temperature decreases the time with the result that glue joints have been cured in a few seconds. It is necessary, therefore, to insure that all parts of a glue joint or glue joints are elevated to at least 75° C. It is quite possible that some parts may get considerably hotter than others. This will have no effect upon the glue so long as the temperature remains below 180° C. In actual practice temperature is kept below 150° C. This flexibility is quite important and allows for the extensive use of high-frequency in complicated wood construction.

Godfrey and Bilhuber[3] have given interesting information regarding the size of machines. The question of the capacity of the machine required is determined by the size, type, variety and spacing of work. The leads of these machines should not run over 10 feet in length. If different presses are to be handled by the same machine, they should be set up so that a minimum of handling will be necessary to reach the electrodes. The weight of the wood placed between electrodes is the prime factor in determining the size of a machine required. If a phenolic resin glue is to be used, the time under pressure should be about 20 min. at 110°C., 10 min. at 125°C. or 5 min. at 135°C. At that rate, bringing the temperature up to 135°C. in a period of 15 minutes, and then permitting it to cool naturally for 15 minutes, allows sufficient heat to insure complete polymerisation of the glue. Since 1 kw. will produce 3413 Btu/hr. using 50 per cent of the input as available power:

$$\text{Output } \frac{3413\times\cdot50}{60}=28\cdot4 \text{ Btu/min./kw.}$$

Using 15 minutes as our operating time,

$$\text{the Btu available } = 28\cdot4\times15 = 426 \text{ Btu}$$

the Btu required to raise 1 lb. of wood from 70° to 280° using ·45 as coefficient of specific heat:

$$\text{we have } 1\times(280-70)\times\cdot45 = 94\cdot5 \text{ Btu,}$$

since 426 Btu are available, a 1-kw. machine could handle

$$\frac{426}{94\cdot5}=4\cdot5 \text{ lb.}$$

Therefore a 1-kw. machine is able to raise 4·5 lb. of wood 210°F. in a period of 15 minutes. If a urea-formaldehyde glue with its lower polymerisation temperature is used as a bond, the amount of wood treated in 25 minutes can be raised to 9 pounds. So long as the electrical capacitance of the work is within the range of the machine, the dimensions of the assembly have no effect upon the heat generated except that full voltage cannot be applied without arcing across the electrodes if the electrodes are too close together. A 5 kw. machine can be used without difficulty and can be easily moved around.

Present moulding methods now are undergoing radical changes. Electrodes can be made as wire, rod, sheet, (both flat and formed) and sprayed metal. Any shape can now be heated successfully with high frequency voltages. Small portable electrodes in the form of a gun are now widely used in "nailing" skins and "ironing" glue joints This "gun" is connected by a long lead to a medium sized transmitting unit operating at approximately 100 megacycles per second and applied with a trigger that is actuated only when power is desired. The gun case is earthed and, therefore, presents no electrical hazard. The amount of heat required to set the glue is obtained in a few seconds.

Moulding with High Frequency. The moulding of plastics parts in most instances requires that a considerable amount of heat be applied to the moulding material. The function of this heat is to soften the material so that it flows and can be pressed into the mould, and also, in some instances, to accelerate the "curing" when applied to thermosetting material. This heat is generally furnished by the mould itself, or from preheating stages occurring just previous to insertion of the material into the mould. Steam, electrical resistance, or induction heaters are the most common sources of heat for both the mould and preheating operations.

It has been found that high-frequency power lends itself ideally to the preheating of many of these moulding materials. There are strong indications that it may have a profound effect on the moulding process.

Method of Applying High Frequency to Moulding. The material to be heated is compressed into preforms and placed between two metal plates which are connected to the source of high frequency. It is essential that these electrodes should always be as large as or larger than the preforms, in order to obtain uniform distribution of power (and heat) through the material. Contact should be as close as possible, although it need not be direct contact. It is very desirable that the electrodes be of the same general shape as the preform. One electrode may be earthed; the other and its associated circuits must be well insulated. The apparatus must be screened as a safety measure. The possible variations in circuits and arrangement of electrodes are admirably shown in a patent of Jarrard, Moritz and Zade.[4] Correct design of electrodes is an essential feature of the process.

Most thermosetting moulding powders have a fairly high dielectric constant and relatively poor power factor in the uncured condition, consequently, the principle of heat generation by condenser losses can be readily utilised in preheating the material.

Dring[2] has considered in some detail the question of using high-frequency heat for moulding. He made it clear that ordinary moulding procedure is severely limited by the poor heating conductivity of moulding powders. In fact, so long as the transfer of heat through the non-conducting mass was the only available method, then any further development of moulding practice seemed unlikely. It was therefore fundamentally important that high-frequency power produced heat in each particle of the moulding powder. The mass of material is uniformly warmed up throughout its bulk. The use of high-frequency heating eliminates problems of thickness. The thickness of the moulding has hitherto been very limited because of the poor heat transfer.

Dring described in particular the benefits of preheating moulding powder or preforms prior to the actual moulding process. The preheating operation is carried out by placing a weighed quantity of moulding powder in a porcelain pot between two metal plates. In this manner a condenser is formed in which the dielectric is made up of the moulding powder. Alternatively, the preforms or pellets can be placed between the metal plates. High-frequency current is then transmitted from a suitable generator. The moulding material becomes uniformly heated very rapidly; the temperature rises rapidly and steadily until the power is switched off. Clearly during this heating procedure, the moulding powder is being cured so that a careful check must be kept on the conditions. At high temperature, e.g. 170°C., the powder will cure very rapidly, whereas at low temperature, say 120°C., the cure will be very slow and the material will be easy to handle.

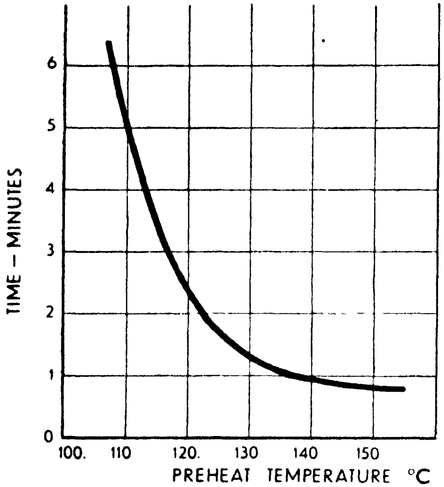


Fig. 249. Relationship between minimum curing time of a 1-inch block and high-frequency preheat temperature

Temperature is taken by inserting a thermocouple needle into the pellet from time to time.

A number of proprietory types of high-frequency equipment are now available. They all offer the same fundamental advantages:

(*a*) Possibility of a shorter curing time,

(*b*) Increased reliability (and control) of the moulding material in the mould.

Time of Cure after High-frequency Preheating. The time of cure in the mould may be considerably reduced. Curing is almost entirely a chemical change, the speed of which depends on temperature. At any single temperature there is a definite time of cure. If all the moulding powder is at the required temperature before going into the mould, the final cure will be the minimum time to complete the chemical action. This should enable articles of any thickness to be cured at the same time. It has been found that high-frequency moulding of a thick article is more effective at the centre than near the surface, which is a complete reversal of present moulding experience. This is important because it tends to eliminate the flaws which are somewhat common. Another outstanding feature arising from preheating by high-frequency methods, is that the moulding material has a much better flow. This fact increases the scope of the moulding. It also tends for better moulding because delicate inserts will not be pushed about to the same extent as in the ordinary procedure.

Dring[2] summarised some of the advantages to be gained from high-frequency preheating as follows:

1. Lower moulding pressures can be used.
2. Easier flow in the tool, cutting down number of powders required with varying flow characteristics.

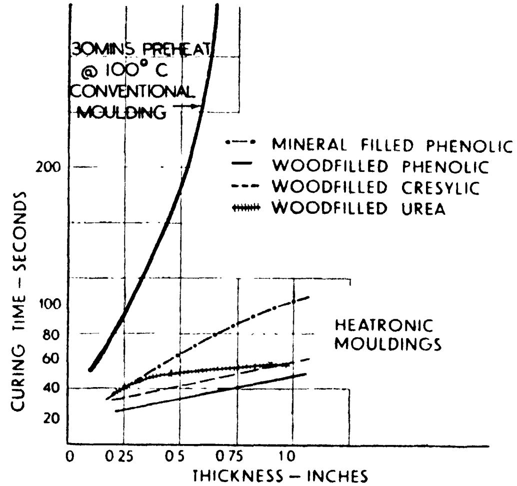


Fig. 250. Relationship between minimum curing time and thickness of moulding

3. Small presses can form larger number of impressions per press.
4. Elimination of cokey sections and the complete consolidation of a whole moulding.
5. Possibility of making more intricate shapes by compression moulding.
6. Shortening of moulding time cycles.
7. Stronger mouldings.

From the point of view of equipment, it is essential that it should be as simple, safe and foolproof as possible. The frequency should be as high as possible so that lower voltages can be used to give the same heat effect. There is a strong trend towards using frequencies of 30, 50 and 100 megacycles. The rough rule for estimating the power required for any job is that 100 watts will heat 100 grams of moulding powder in 2½ minutes through the temperature rise of 100°C.

There is still some difference of opinion concerning the best form of high-frequency equipment. On the one hand it is thought that large units of the order of several kilowatts should be used to serve a number of presses. Yet another group are of the opinion that a small unit of e.g. 500 watts should be used to serve each individual press.

Based on extensive experiment, Witty[8] has reached the following conclusions about the merits of high frequency moulding.

1. *Saving of Time.* A possible 50 per cent saving in the closing and curing portions of the mould cycle can be easily obtained. If press procedure and handling routine are specially arranged for rapid preheating by radio frequency power, possibly a much greater time saving could be realised. This saving will manifest itself as increased production with fewer presses.

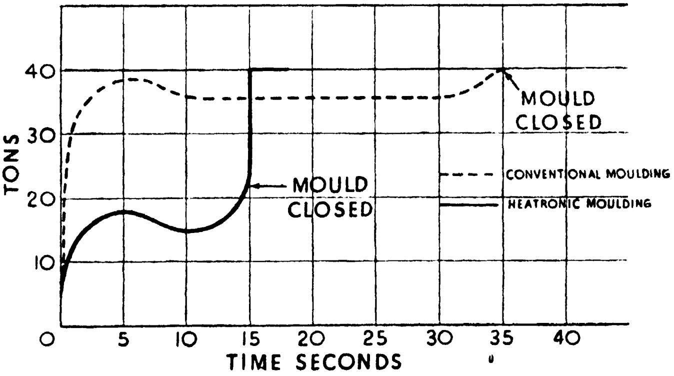


Fig. 251. Curves showing closing time and closing pressure for (*a*) conventional moulding, and (*b*) heatronic moulding

2. *Improvement of Product.* Uniform heating throughout the preform not only results in a more thorough polymerisation of the impregnated material, but should also tend to improve quality from the standpoint of residual stresses and consequent warpage or physical distortion. Also, less expensive moulding compounds containing less resin but yielding satisfactory finished pieces may be possible.

3. *Mould Stresses.* Another obvious advantage of preheating the moulding material to a plastic state before insertion into the mould is the decreased stress on the moulded parts. This is particularly true of intricate moulds in which comparatively delicate inserts are placed. These are quite often broken off because of side pressures to which they are subjected by the semi-plastic material flowing into the recesses of the mould.

4. *Thick Sections.* Because of its ability to heat uniformly through the material, radio frequency power is particularly well adapted to preheating thick sections or large preforms. Conventional oven heating is necessarily slow, because of the relatively poor heat conductivity of the material. Higher oven temperatures are likely to result in case hardening of the preforms due to excessive surface heat.

Mouldings of unusual thicknesses, several inches thick, have been produced by this method. Examination has shown that curing has occurred right through, a feature which would be extremely difficult to attain by conventional methods even after lengthy heating.

Considerable experimental work has already been carried out, with most encouraging results.

The advantages of moulding normally difficult materials with the aid of high-frequency heating have been summarised by Meharg:[6]

1. Moulding of thermosetting impact-resistant phenolic materials, when preformed, can be accomplished as easily as the moulding of general-purpose wood-filled phenolic materials. This should widely increase the use of the impact-resistant materials.

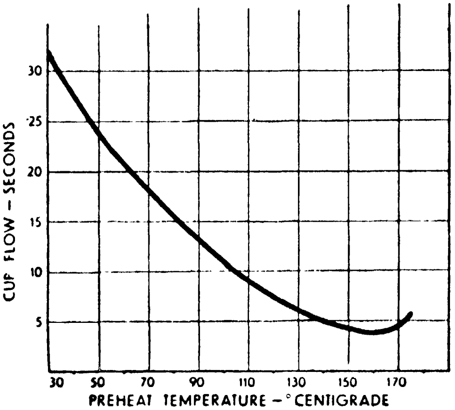


Fig. 252. Curve showing variation of cup flow with high-frequency preheat temperature

2. Moulding of thermosetting materials in $\frac{1}{8}$-in. thickness and greater can be accomplished in cycles as short or shorter than the cycles for thermoplastic materials on injection moulding machines.

3. Moulding pressures may be reduced by 30 to 40 per cent as compared to those necessary for the present methods of moulding.

4. Curing time may be shortened to from one-tenth to half the time used in present methods of moulding.

5. For the first time it becomes commercially practical to mould pieces thicker than three-eighths of an inch from thermosetting materials. Meharg showed that the rate of cure is almost independent of thickness.

The Use of High-Frequency Heating for Thermoplastics. The use of high-frequency heating has proved extremely useful for handling cellulose plastics, polyvinyl chloride, its copolymers, methyl methacrylate polymers and certain other thermoplastics.

The method facilitates:

(*a*) The welding together of thermoplastics.
(*b*) Softening of materials to get them into a condition suitable for further processing.
(*c*) Softening materials to enable them to retain inserts, etc.

Jarrard, Moritz and Zade[4] have recently described many aspects of handling thermoplastic materials by high-frequency heating.

Polyvinyl chloride in particular is a difficult material to weld or join, because it is (*a*) sensitive to heat, (*b*) impervious to solvents, (*c*) it has poor adhesive properties. Joins are frequently necessary, for example, in making cables, tubes, etc., either as part of the processing or for repairs. Much difficulty has attended this operation. If the material is held for any length of time above 160°C., it tends to decompose. On the other hand, the range of temperature in which it can be welded is comparatively small and close to the decomposition temperature. Because heat transmission is so poor, it is extremely difficult to get heat uniformly distributed through any thickness of material.

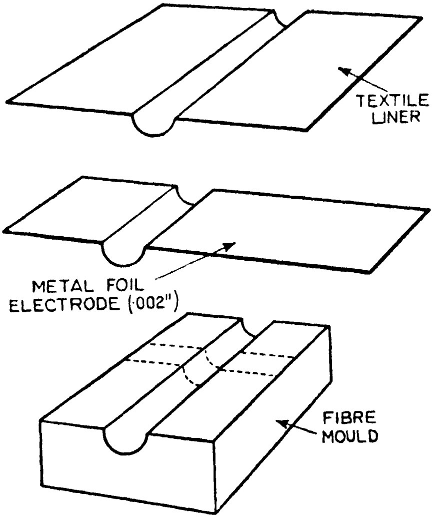


Fig. 253. Half of mould used to repair polyvinyl chloride covered cable. The portions fit together with cable in the cavity

High-frequency methods have proved extremely effective in this field of activity. Some have been described by Walton, Quayle and Jones[7] in recent patents. The chief feature is the ability to secure the extremely rapid rise in temperature throughout the material. The heat generated is developed uniformly throughout the mass, irrespective of the thickness. The principle method is to pass a fairly high current at a high frequency of 20–200 megacycles per second through the material, while applying mechanical pressure to it.

The power loss in plasticised polyvinyl chloride at frequencies above 20 megacycles per second enables the temperature to rise to welding conditions in a few seconds. This is, uniform temperatures from 150° to 180°C. are attained in a few seconds by the use of comparatively low voltage.

This rapid generation of heat permits an extraordinary speed of welding. The conditions cannot be equalled by other heating methods. All heat is generated only in the material. The surrounding moulds or retaining tapes remain cool, and can be removed immediately welding is completed. The use of heat insulating moulds or tapes gives maximum effects and permits the immediate opening of moulds as soon as the high-frequency field is switched out.

The method has been successfully utilised in the repairing of polyvinyl chloride; a technique has been developed and equipment constructed for routine handling by semi-skilled personnel of factory repairs on a wide range of cables.

In these applications the cable conductor serves as one electrode, while the other electrode is mounted in a mould. One typical set-up is shown in Fig. 253. Actually, moulds are not strictly necessary, for such jobs can be taped and then surrounded by a spring-loaded clamp in which the sheet metal electrode is mounted.

Very simple units have already been developed for jobs of this description. Since the amount of material involved is small, relatively little power is involved, so that one such unit can even be worked by an ordinary car battery.

The advantages of the method are very apparent.

High-Frequency Repairing.

(*a*) No preheating or final cooling necessary. Moulds are cool enough to handle immediately.
(*b*) Moulding time is of the order of 10–30 seconds.
(*c*) Adequate high temperatures very rapidly attained with uniform heating.
(*d*) Fusion occurs throughout the material.
(*e*) Speed of welding and cool moulds prevent loss of plasticiser.
(*f*) Flow and decentralising is prevented by using extended moulds.
(*g*) Energy is only used when required. There is no waste through "idling."

The Use of High-Frequency Heating in Sealing Plastics. The spreading use of plastics-coated fabric for application as raincoats, tarpaulin, packaging, etc., has raised the difficulty of joining edges. With polyvinyl chloride and copolymers, the usual procedures of stitching, cementing or heat sealing all present difficulties. Heat sealing, which appears to be the most desirable method, has not been too satisfactory by ordinary procedures.

High-frequency heating is now being widely used for heat-sealing thermoplastic materials. Moreover, the trend is strongly set for further developments. Two methods are used: .

(*a*) Passing the materials to be bonded between rollers which serve as the electrodes.

Brown[1] described the method of heat-sealing seams by utilising high-frequency heating. The overlapping edges of the material are run between two small rollers. These two metal rollers serve as electrodes for a small high-frequency field. Heat is generated in the material and a perfect weld is obtained as the edges soften and fuse together. The bond is claimed to be watertight and airtight.

This procedure is being used for example,, in making raincoats from PVC sheets. The bonded seams are most effective. The only drawback at present is that the speed of welding is still much slower than ordinary stitching.

(*b*) Use of shaped electrodes to heat-seal specific articles.

In this instance the electrodes are designed to correspond with the actual seal which is to be formed. The thermoplastic sheets are placed between the two electrodes, which are then clamped or pressed down at low pressures. The high-frequency current is then switched on for a few seconds, during which the actual seal is made. While at first quite small articles were made in this way, such as tobacco pouches, the maximum size manageable grows steadily.

REFERENCES

1 BROWN. *Plastics*, 1943, **7**, 349.
2 DRING. *Plastics*, 1944, **8**, 10.
3 GODFREY AND BILHUBER. *Modern Plastics*, September 1943, p. 89.
4 JARRARD, MORITZ AND ZADE. B.P., 555,054/1943.
5 LEDUC. *Rev. Gen Caoutchouc.* 1935, **18**, 115; 1935. *Proc. Rubber Tech. Conf.*, 1938, p. 381.
6 MEHARG. *British Plastics*, 1943, **15**, 6.
7 WALTON, QUAYLE AND JONES. B.P., 554/176; 554,854/1943.
8 WITTY. *Chem. Met. Eng.*, 1943, April, p. 80.
9 BRAJNIKOFF. *Plastics*, 1942, **6**, 373.

CHAPTER XXXI

ANALYTICAL ASPECTS OF PLASTICS

It is quite evident that with so many different chemical types of plastics, systematic analysis must be a very complicated difficult matter. Comparatively few investigators have faced the fearsome task of organising a comprehensive scheme. In the main the available information is somewhat scattered, evolved by specialists working in each particular field of activity. Some of these have already been described in chapters dealing with individual synthetic resins. There is little difficulty in identifying the raw synthetic resins or other plastic bases in their pure state. In most cases visual observation is sufficient. It becomes somewhat troublesome in the case of some of the vinyl compounds which are white powders.

It is proposed here to describe briefly the more organised indentification schemes.

Nechemkin[6] has outlined a procedure for the identification of common commercial plastics.

He is particularly interested in the different odours emitted by plastics when heated strongly. A strip or small rod of the material is held in a small flame, removed if it catches fire, otherwise allowed to heat for not more than 10 seconds.

Procedure. The plastic, in strip or rod form, if possible, is held at one side of a Bunsen flame until it takes fire, but not more than 10 seconds. The following scheme is then consulted:

TABLE 165

I. No flame is produced. The article retains its shape. The odour of formaldehyde is present in all cases.

- *A.* No other odour; urea-formaldehyde.
- *B.* Strong fish-like odour; melamine-formaldehyde.
- *C.* Phenolic odour; phenol-formaldehyde.

II. The burning plastic extinguishes itself on removal from the Bunsen flame. Specimen held just to edge of flame.

- *A.* A green zone is produced.
    - 1. Odour of burnt rubber.
        - (*a*) Green area pronounced: pliofilm.
        - (*b*) Green area small and overshadowed by yellow: neoprene.

        2. Odour acrid but not that of burnt rubber: vinyl chloride derivative.
        3. Odour sweet, heavy black ash: vinylidene chloride resins.
    - *B.* Odour of burnt milk protein: casein.
    - *C.* Sparks from flame of burning plastic and acetic odour: cellulose acetate.

III. The plastic continues to burn after removal from the Bunsen flame. Flame examined for colour during the first second of burning.

- *A.* Burning very rapid and intense white flame.
    1. Odour of camphor: celluloid.
    2. No camphor odour: cellulose nitrate.
- *B.* Flame predominantly blue, may have a small white tip.
    1. Very strong sweet floral fruity odour: methacrylate.
    2. Odour reminiscent of burning vegetation or fresh celery. Flame is almost entirely blue. The resin is soluble in aqueous 60 per cent (by volume) hydrochloric acid: nylon.
    3. Weak very slightly sweet odour: polyvinyl formal.
    4. Odour of rancid butter or cheese.
        - (*a*) Sparks produced from flame of burning plastic: cellulose acetobutyrate.
        - (*b*) No sparks, burning smooth and steady: polyvinyl butyral.
- *C.* Flame surrounded by bright green mantle, odour of burnt rubber: plioform.
- *D.* Flame surrounded by a purple mantle, sparks and an acetic odour: polyvinyl acetal.
- *E.* Flame yellow-white and luminous.
    1. Odour of butyric acid: cellulose acetobutyrate.
    2. Odour of burnt milk protein: casein.
    3. Sweet floral odour: (marigold), flame smoky: polystyrene.
    4. Weak very slightly sweet odour: polyvinyl formal.
    5. Odour of burnt paper: cellulose.
    6. Odour of burnt rubber, flame weak, small green mantle overshadowed by yellow. White flashes may appear in the flame: neoprene.
- *F.* Flame surrounded by yellow-green mantle.
    1. Burns with difficulty and sparks, producing an acetic odour; the melted burning plastic, when allowed to drip into water, produces heavy black-brown foamy granules or flakes: cellulose acetate.
    2. Burns readily once started, producing a slight sweet odour. The melted burning plastic, when allowed to drip into water, produces flat discs which are light tan when the plastic is clear, or not very different in colour from the original plastic when the plastic is coloured: ethyl cellulose.

Examination of raw materials by ultra-violet light brings out a number of differences. However, it is ineffective in compounds where the presence of plasticisers, fillers, etc., confuses the issue.

TABLE 166

FLUORESCENCE IN ULTRA-VIOLET LIGHT

Material	
Phenol-formaldehyde (no filler)	Green
Phenol-formaldehyde (wood flour filler)	Blue Violet
Phenol-formaldehyde (mineral filler)	Blue Violet
Phenol-formaldehyde (scrap fabric filler)	Blue Violet
Phenol-formaldehyde (paper laminated)	Blue Violet
Phenol-formaldehyde (fabric laminated)	Blue Violet
Phenol-formaldehyde (asbestos laminated)	Blue Violet
Phenol-formaldehyde (cast)	Blue Violet
Phenol-formaldehyde (glass fabric laminated)	Blue Violet
Phenol-furfural (wood flour filler)	—
Urea-formaldehyde (moulded)	Blue White
Melamine (filled)	—
Cellulose acetate (sheet)	Pale Blue
Cellulose acetate (moulded)	Pale Blue
Cellulose acetate butyrate	—
Cellulose nitrate	Yellow Brown
Ethyl cellulose	—
Polystyrene	Blue Violet
Polythene	Blue White
Polyvinyl chloride	Brownish Blue
Polyvinyl chloride-acetate (no filler)	—
Polyvinyl chloride-acetate (filled)	—
Polyvinyl formal	Whitish Blue
Polyvinyl butyral	—
Polyvinyl alcohol	Light Blue
Polyvinylidene chloride	—
Methyl methacrylate (cast)	Bright Blue
Methyl methacrylate (moulded)	Bright Blue
Nylon	Bluish White
Casein	White
Glyptals	Light Blue

Table 167

Specific Gravity and Specific Volume of Plastics

Material	Specific Gravity	Specific Vol. (cu. in./lb.)
Phenol-formaldehyde (no filler)	1·28	21·7
Phenol-formaldehyde (wood flour filler)	1·25–1·52	22·2–18·2
Phenol-formaldehyde (mineral filler)	1·59–2·09	16·4–13·3
Phenol-formaldehyde (scrap fabric filler)	1·37–1·40	20·2–19·8
Phenol-formaldehyde (paper laminated)	1·30–1·40	21·3–19·1
Phenol-formaldehyde (fabric laminated)	1·30–1·40	21·3–19·1
Phenol-formaldehyde (asbestos laminated)	1·55–1·80	17·8–15·0
Phenol-formaldehyde (cast)	1·27–1·32	21·8–20·0
Phenol-formaldehyde (glass fabric laminated)	1·4 –1·6	19·7–17·3
Phenol-furfural (wood flour filler)	1·30–1·40	21·3–19·8
Urea-formaldehyde (moulded)	1·45–1·50	19·1–18·5
Melamine (filled)	1·5 –1·9	—
Cellulose acetate (sheet)	1·27–1·38	21·8–20·2
Cellulose acetate (moulded)	1·27–1·38	21·8–20·2
Cellulose acetobutyrate	1·20–1·22	22·8–23·1
Cellulose nitrate	1·35–1·60	20·5–17·3
Ethyl cellulose	1·14	24·3
Polystyrene	1·05–1·07	26·3–25·8
Polythene	0·93	—
Polyvinyl chloride (plasticised)	1·20–1·60	23·0–17·3
Polyvinyl chloride-acetate (no filler)	1·34–1·36	20·7–20·1
Polyvinyl chloride-acetate (filled, moulded)	1·35–2·50	20·5–11·1
Polyvinyl formal	1·23	—
Polyvinyl butyral	1·10	—
Polyvinyl alcohol	1·26	—
Polyvinylidene chloride	1·6 –1·75	17·3–15·8
Methyl methacrylate (cast)	1·19	23·2
Methyl methacrylate (moulded)	1·18	23·4
Nylon	1·06–1·19	26·0–23·2
Casein	1·34	20·5

A very comprehensive scheme for identification has been described by Mark and Rath.[5] They base much of their work on dry distillation, recommending about 1 gm. of sample in a standard test tube. Gaseous products are caught in another test tube and examined quantitatively. The behaviour of the sample is also tested.

TABLE 168
BEHAVIOUR OF SAMPLE ON DRY DISTILLATION

Behaviour of the Sample	Substances
Sample remains colourless and evolves volatile monomers. Condensed liquor invisible on the wall of the tube. Later sample gets yellow	Polystyrene (characteristic smell of monostyrene). Polyisobutylene Polyethylene Polyacrylic (methacrylic) esters (characteristic acidic smell of monomers) Polyvinyl esters (acidic smell)
Sample decomposes gradually without distillation, but fume-like products are evolved. Later solid turns yellow	Chemical investigation of decomposition is mentioned under Table 169
Sample sublimes in white crystalline needles	Phthalic acid condensation products
Sample blows up	Nitro-cellulose with high nitrogen content

TABLE 169
DECOMPOSITION PRODUCTS ON DRY DISTILLATION

Evolved Gases and Fumes show following Reaction		Substances
Acid Reactions	Precipitate of cloudiness with $AgNO_3$	Polyvinyl chloride, polyvinylidene chloride
	Reacts with nitron	Nitro-cellulose
	Presence of acetic acid	Polyvinyl acetate, cellulose-acetate
	Other organic acids formed	Polyvinyl and cellulose esters
Alkaline Reactions	-	Condensation products of aldehydes with urea, melamine, aniline or proteins

TABLE 169—*continued*

CLASSIFICATION ACCORDING TO SAPONIFICATION NUMBER

Saponification Number	Group	Substance	Behaviour
Below 20	Polymeric hydrocarbons		
		Polystyrene	Depolymerises above 310° C. to monostyrene (characteristic smell) gives dibromostyrene (mp. 74°) with Br_2 and benzoic acid with HNO_3
	Polyhydroxyl compounds	Polyvinyl alcohol	Soluble in water; iodine in acid aqueous solution gives characteristic blue odour
		Phenol-formaldehyde condensation products	Heating with alcoholic KOH and diazotised nitro-aniline gives a red dyestuff; A- and B-state are soluble and show high hydroxyl content; C-state insoluble and with difficulty swellable
	Poly-ethers	Cellulose-ether	Methylcellulose: soluble in cold water, precipitates upon heating. Ethyl cellulose: insoluble in water, soluble in organic solvents. Alkoxyl groups can be determined according to Zeisel. Benzylcellulose: splitting off of the benzyl group as benzylacetate with acetic anhydride and sulphuric acid
	Polyvinyl formals and acetals	Polyvinyl aldehyde condensation products	One splits off the aldehyde by boiling with 25% H_2SO_4, distils over and identifies with fuchsin reagent; the remaining polyvinyl alcohol is identified as described above. The aldehyde can be determined quantitatively by converting it into the oxime and titrating the HCl produced by the hydroxylamine hydrochloride

TABLE 169—*continued*

CLASSIFICATION ACCORDING TO SAPONIFICATION NUMBER

Saponification Number	Group	Behaviour
From 20 up to 200	Phenolformaldehyde resin condensation products	Are difficult to saponify (up to 24 hours); heating may be necessary; saponification numbers are between 140 and 160. Phenol can be determined by coupling with diazonium salt
Above 200	Cellulose-acetate, -propionate, -butyrate and mixed esters	After saponification with phosphoric acid or alcoholic KOH, the acid is distilled over and identified (colour reactions, titration). Regenerated cellulose remains behind (X-ray diagram, solubility in CuO—HN_3)
Above 200	Polyvinyl-acetate, -propionate, -butyrate	Gives green to blue colour with acetic anhydride and H_2SO_4. After saponification with alcoholic KOH the acid is distilled over and determined. Polyvinyl alcohol is identified by solubility in water and precipitation with alcohol
	Polyacrylic-ester (methyl, ethyl, propyl, butyl)	Depolymerise easily above 290°; monomeric ester distils over; shows characteristic smell. After saponification alcohol can be determined
	Polymethacrylic-ester (methyl, ethyl)	Depolymerises easily above 300°; monomer distils over, proves a characteristic smell. Reduction of methacrylic acid with sodium amalgam or zinc dust in acid solution yields isobutyric acid (definite smell)

TABLE 169—*continued*

CLASSIFICATION ACCORDING TO SAPONIFICATION NUMBER

Saponification Number	Group	Behaviour
Above 200 (*continued*)	Phthalic acid-glycerol esters	Give white sublimate upon heating. Phthalic acid can be identified as fluoresceine (heating with resorcinol and sulphuric acid) or as K-with alcoholic KOH. It must be noted, however, that plasticisers often contain phthalic acid esters. They have to be extracted with ether or petrol. Quantitative determination of phthalic acid through the K-salt, which is insoluble in alcohol. Phthalic acid can also be extracted from the alkaline saponification liquid with ether and titrated. Glycerol according to Willstaetter and Medinavetia
	Phthalic acid-fatty acid-glycerol esters	After saponification, fatty acids are extracted with benzene and identified by acid and iodine number. Phthalic acid and glycerol as above

Saponification Number.[5] The saponification number of resins has been used by Mark and Rath in their analysis procedures. The value is limited to virtually pure materials because plastic compositions contain many ingredients which may be saponified.

The usual method employed to determine the saponification number is to treat a finely ground weighed sample with an excess of normal sodium hydroxide in methyl alcohol. The excess alkali after saponification is estimated by titrating with normal acid solution using phenolthalein as indicator. In cases where a high saponification value is found the acid present can be separated and examined further. A saponification value greater than 200 suggests the presence of polybasic esters.

One of the first routine tests to which plastics, in common with other materials, are subjected, is to find what non-metallic elements are present, i.e. whether chlorine, nitrogen, sulphur or phosphorus are there.

TABLE 170—CLASSIFICATION ACCORDING TO N, S, P, AND Cl CONTENT

Presence	Substance	Identification
Nitrogen only	Nitro-cellulose	X-ray diagram and fluorescence. Denitration with Na_2S_2 and identification of cellulose. Saponification and detection of HNO_3 with diphenylamine. Characteristic solubility of nitrocelluloses of different N-content in alcohol-ether, butyl acetate, acetone
	Urea or melamine formaldehyde resins	Heating with 25% sulphuric acid yields formaldehyde, identify with fuchsine reaction. Nitrogen content according to Kjeldahl
	Polyacrylonitrile	Polyacrylonitrile is hardly ever used as such (N-content 26%). If so it depolymerises above 300° and gives off small amounts of HCN
	Aniline-formaldehyde resins	Heating with 20% sulphuric acid splits off aniline; the acid solution is diazotised and coupled with R-salt solution. Bright red colour proves the presence of aniline
Chlorine only is present	Polyvinyl-chloride	Characteristic X-ray diagram. High chlorine content (pure polyvinyl chloride 53-55% Cl; after-chlorinated samples 64-66% Cl; copolymers with vinylacetate and acrylic esters 43-47% Cl)
	Polyvinylidene chlorine	Characteristic X-ray diagram; chlorine content around 70%
Nitrogen and Sulphur	Thiourea-formaldehyde resins	Give a very sensitive and specific reaction with Cu-salts and potassium ferricyanide
Nitrogen, Sulphur, Phosphorus	Protein-formaldehyde resins	Dry distillation gives a characteristic smell. Extract a sample with sulphuric acid and titrate the extract with permanganate. More permanganate is used up than by natural horn. It must be understood that phosphoric acid esters are often used as plasticisers and that P-content in an unextracted resin may be due to their use

TABLE 171—A SCHEME FOR THE QUALITATIVE

BASED ON SOLUBILITIES

II. CLEAR, COLOURLESS OR COLOURED, SOLID PLASTICS

A. Reflux a large sample of the finely

Undissolved Residue

Phenolics, urea and other amine plastics, alkyds, polystyrene, polyvinyl chloride, polymethyl methacrylate, benzyl cellulose, cellulose nitrate, cellulose acetate

Treat with benzene, and reflux

Residue	Solution in Benzene
Phenolics, ureas, alkyds, polyvinyl chloride, cellulose nitrate, cellulose acetate	Polystyrene, polymethyl methacrylate, benzyl cellulose, and mixed polymers of esters of polyacrylic acid with polyvinyl chloride

Apply the seven tests listed under Part I to be applied to residue insoluble in toluene and in methyl formate

Also treat with methyl formate and reflux

Residue	Solution
Phenolics, ureas, glyptals, polyvinyl chloride	Cellulose nitrate, cellulose acetate, part of the polyvinyl chloride and part of the glyptals

Distil off the solvent and treat the residue with amyl formate (boiling point 116° C.)

Residue	Solution
Cellulose acetate (saponify and test for acetic acid)	Cellulose nitrate. Distil off the solvent. The residue is highly flammable and gives the characteristic diphenyl amine test

Naturally, it must be borne in mind that ingredients other than the plastic materials will show the presence of these elements, e.g. plasticisers, fillers, etc.

The usual method is to subject a sample to fusion with sodium. The resulting material is then extracted with water. A little silver nitrate solution is added to a portion of this extract. A white precipitate of silver chloride indicates the presence of chlorine.

Nitrogen. Part of the aqueous extract from sodium fusion is warmed with ferrous sulphate and sodium hydroxide. It is then made acid by

Analysis of the More Common Plastics[3]
—continued

Moulded or Extruded (without Fillers)

powdered plastic with methanol

<table>
<tr><th colspan="3">Solution in Methanol</th></tr>
<tr><td colspan="3">Ethyl cellulose, plasticisers
Add an excess of benzene (petroleum ether)</td></tr>
<tr><th colspan="2">Precipitate</th><th>Solution</th></tr>
<tr><td colspan="2">Ethyl cellulose (identified by the presence of the C_2H_5O group)</td><td>Plasticisers</td></tr>
<tr><td colspan="3">Treat with ethyl alcohol and reflux</td></tr>
<tr><th colspan="2">Residue</th><th>Solution</th></tr>
<tr><td colspan="2">Polystyrene, benzyl cellulose (and portions of mixed polymers)
Treat with ether</td><td rowspan="3">Polymethyl methacrylate (and portions of mixed polymers)
Test by observing the low specific gravity (1·18) and after depolymerising the substance by saponifying the distillate at from 95° to 105°C. and reducing the liberated methacrylic acid to isobutyric acid</td></tr>
<tr><th>Residue</th><th>Solution</th></tr>
<tr><td>Benzyl cellulose (test to identify)</td><td>Polystyrene. Sp. gr. about 1·05. Test solubility, and test by heating</td></tr>
</table>

the addition of hydrochloride acid and a few drops of ferric chloride solution is added. A typical prussian blue precipitate or blue-green-colour indicates the presence of nitrogen.

Sulphur. When sulphur compounds are heated with sodium, sodium sulphide is formed and is present in the aqueous extract. A little sodium nitro-prusside solution is added and a brilliant red coloration indicates the presence of sulphur.

The aqueous extract from the sodium fusion will also tarnish a bright silver coin, going black if sulphur is present.

The lead acetate solution will give a black precipitate of lead sulphide when added to the solution.

Phosphorus. A small sample of the material is heated in fuming nitric acid to about 150° C. When phosphorus is present it is oxidised to phosphoric acid and addition of ammonium molybdate gives a typical precipitate indicating phosphorus.

Fischer[3] has outlined a complete system for the qualitative analysis of almost any sample of plastic material, in any of the numerous forms likely to be encountered. It is based on the selective solubilities of the various synthetic bases. The procedure is clearly defined in Tables 171 and 172.

The water content of plastic materials is a matter of importance since it will have a profound influence on processing characteristics. The method employed for almost every type of plastic is similar. It is as follows: About 50 grams of finely ground plastic is placed in 100 grams of freshly distilled xylene. This mixture is distilled, the aqueous fraction being collected in a graduated tube so that the quantity is read off directly.

Analysis of Phenolic Resins. Phenolic resins are of course based on phenol, cresol, formaldehyde, furfural, and so on. As already indicated, there is a wide variety of other ingredients which may be incorporated, and which at some time or other may need to be analysed. Since phenolic resins are used for a variety of purposes, mouldings, laminated, materials, adhesives and coatings, etc., the subject has many possibilities. There is also the aspect of checking up on moulding powders as well as finished mouldings.

Phenolic articles are usually made in some dark shade. Cast phenolic resins will, of course, exist as transparent material, and in all colours. Phenolic resins and their mouldings in the usual way have a phenolic odour which becomes more pronounced when they are warm. Except in the case of coating materials, which may be oil soluble types containing rosin or fatty acids, they will not be saponifiable.

Apart from odour there are a number of methods for establishing the presence of phenol. Phenol, if present, may be extracted by boiling the ground material with water. Alternatively, the material can be heated in a sodium hydroxide solution. Another procedure is to fuse it with caustic soda or soda lime and then add acid. The presence of phenolic bodies will be evident from the odour.

The solution containing phenol if acidified with sulphuric acid, boiled, and then a little Millon's reagents added, gives a red colour. Alternatively, if a solution of sulphuric acid containing 1 per cent formaldehyde is carefully added to the solution, a red ring will be formed where the two liquids meet.

Table 172—A Scheme for the Qualitative Analysis of the More Common Plastics.[3] Based on Solubilities

I. Opaque, Homogeneous or Laminated Plastics, Moulded or Extruded

A. Treat a large sample of the finely ground plastic with toluene, and reflux

<table>
<tr><td colspan="3">Residue Insoluble in Toluene</td><td colspan="6">Solution in Toluene</td></tr>
<tr><td colspan="3">Phenolics, casein and other protein plastics, urea and other amine plastics, cellulose hydrate, cellulose nitrate, cellulose acetate, polyvinyl chloride. Also inorganic and organic fillers and colouring matters and glyptals and other alkyds</td><td colspan="6">Ethyl cellulose, benzyl cellulose, polystyrene, polyacrylic acid-methyl ester, methyl methacrylate, mixed polymers of methyl acrylate and polyvinyl chloride, coumarone resin, bituminous material, chlorinated rubber and plasticisers</td></tr>
<tr><td colspan="3">Drive off the toluene from the above mixture by warming over a water bath, and treat the residue with methyl formate, refluxing the mixture</td><td colspan="6">Distil off the toluene by slow heating over a water bath until the mixture is toluene-free. Then treat with methanol and relux</td></tr>
<tr><td>Insoluble in Methyl Formate</td><td colspan="2">Soluble in Methyl Formate</td><td colspan="4">Residue insoluble in methanol</td><td colspan="2">Soluble in methanol</td></tr>
<tr><td>Phenolics, casein, urea, glyptals, cellulose hydrate, polyvinyl chloride, fillers and colouring matters</td><td colspan="2">Cellulose nitrate, and cellulose acetate</td><td colspan="4">Benzyl cellulose, polystyrene, polyacrylic acid, methyl methacrylate, mixed polymers, coumarone resin, bituminous material, chlorinated rubber</td><td colspan="2">Ethyl cellulose and plasticisers
Add petroleum ether in excess</td></tr>
<tr><td rowspan="6">Other tests to be applied to above residue:
1. Phenol: Heat with NaOH. Odour of phenol and characteristic colour reactions identify it
2. Amine plastics (urea, thio-urea, etc.). Heat with NaOH. Odour of ammonia identifies them. Test for S to see if thiourea is present
3. Protein plastics (casein, etc.). Destructive distillation gives odour of burning hair or feathers. Heating with NaOH gives odour of ammonia
4. Glyptals: Test for phthalic acid
5. Cellulose hydrate: smell of burning paper on charring
6. Polyvinyl: Test for Cl.
7. Fillers, Inorganic: Reduce plastic to ash and test qualitatively. Examine microscopically. Use phloroglucinol test for lignin to determine presence of wood</td><td colspan="2">Distil off the solvent and treat the remainder with amyl formate (boiling point 116°C.)</td><td colspan="4">Treat with ether</td><td>Precipitate</td><td>Solution</td></tr>
<tr><td>Residue</td><td>Solution</td><td colspan="2">Residue</td><td colspan="2">Ether Solution</td><td rowspan="5">Ethyl cellulose. Further identified by tests for the ethyl group, and tests of solubility</td><td rowspan="5">Plasticisers. After distilling off the solvent, make tests for the more common plasticisers. Camphor chlorinated diphenyl, tricresyl phosphate</td></tr>
<tr><td rowspan="4">Cellulose acetate. Test for acetic acid by saponification</td><td rowspan="4">Cellulose nitrate. After distilling off the solvent, test the flammability and makes the diphenylamine test</td><td colspan="2">Benzyl cellulose, mixed polymerisation product as above, chlorinated rubber, bituminous materials in part</td><td colspan="2">Polystyrene, coumarone resin, mixed polymers in part, bituminous materials in part</td></tr>
<tr><td colspan="2">Treat with methyl formate</td><td colspan="2">Distil off the ether and extract the residue</td></tr>
<tr><td>Residue</td><td>Solution</td><td>Residue</td><td>Solution</td></tr>
<tr><td>Chlorinated rubber and polyvinyl chloride (mixed polymerisation). Give test for chlorine. Bituminous materials give residue a dark brown colour</td><td>Benzyl cellulose and part of mixed polymers. Test for benzene cellulose by distilling off solvent, treating with dilute H_2SO_4 and heating. Odour of benzaldehyde, disappearing on neutralising with NaOH identifies it</td><td>Polystyrene (test to identify.) Part of mixed polymers</td><td>Coumarone resin
Distil off the solvent, saponify with alcoholic KOH. Test the unsaponifiable matter by Storch-Morowsky test</td></tr>
</table>

Acetone Extract. Almost certainly the most important routine test on phenolic mouldings is the acetone extraction. This is a criterion of the degree of cure of a product. It is carried out in the following manner:

A moulded article is taken and filed, so that the particles pass through a No. 30 B.S. sieve, and not through a No. 60 B.S. sieve. Between 6 to 8 grams of powder is dried in a vacuum dessicator for 18 hours. Five grams of the dried powder is extracted in a Soxhlet Extraction apparatus for 6 hours with acetone. Thereafter the thimble is dried to constant weight and weighed. The loss in weight represents the amount extracted by acetone. This should not exceed 6 per cent.

Other practical limits for moulded articles include:

Free phenol not more than 1·5 per cent.
Free formaldehyde not more than 0·05 per cent.
Free ammonia should not exceed 0·1 per cent.

It is found in practice that most articles of any appreciable thickness are not fully cured; in other words, they give an appreciable acetone extract. In thick articles, for example, the acetone extract is found to be greater at the centre of the article than at the outside. It is of some interest in this connection to note that thick mouldings which have been preheated by high-frequency methods, and thereafter set, show much more complete cure, as indicated by extremely low acetone extract values.

Phenolic resins, especially moulding powders and their mouldings, may contain a very wide variety of ingredients such as catalytic agents, lubricants, fillers, acids, and so on. Some of these, such as ammonium salts, hexamethylene tetramine, etc., are soluble in water and can be extracted. Thereafter both the water extract and the residue can be subjected to routine analysis.

Examination of Solids. The solid residue may contain a wide variety of organic and inorganic fillers, etc. Organic fillers such as wood flour, cellulose, textiles, etc., can readily be observed under the microscope.

Inorganic fillers will be determined by reducing the residue to ash by ignition in a crucible, and subjecting the ash to routine chemical analysis. The aqueous extract from a moulding powder is obtained by grinding finely some of the solid material. A weighed quantity is extracted in ten times its weight of boiling distilled water which is then filtered. The solution is then subjected to a number of tests, some of which are described in the following survey.

Tests on Phenol. Phenol, C_6H_5OH, is sold on the basis of its purity and as the presence of any impurity causes a lowering of the melting point in proportion to the amount present, this latter characteristic forms a valuable criterion as to the purity of the product. The method has been severely criticised. It is known that absolutely pure 100 per cent phenol crystals melt at 41·00° C. Commercial phenol such as is used for the manufacture of resins can now be obtained in such a high state of purity that it has a melting point of 40·7 to 40·8° C., i.e. it contains 99·7 per cent phenol.

The crystallising point is determined in the following way:

The temperature of the sample is raised till a thermometer suspended in the vapour reads 180° C. If this heating is done in a tube the moisture can be seen rising as a ring of vapour. The dried sample is allowed to cool, a cork carrying a calcium chloride tube being inserted in the mouth of the tube to prevent reabsorption of water vapour. Cooling is continued till crystallisation occurs at which point the temperature remains constant, due to the evolution of latent heat. Tables have been prepared from which the purity of the phenol can be read straight off.

Phenol. The leading chemical process for estimating phenol is the Koppeschaar method. This is based on the bromination of phenol in aqueous solution. It can also be carried out to determine free phenol in the aqueous extract obtained from moulded resins.

$$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr.$$

When phenol is treated with excess of bromine it is quantitatively converted into tribromophenol. Addition of potassium iodide results in the liberation of iodine equivalent to the excess of bromine present. The iodine is titrated in the usual manner with sodium thiosulphate solution.

$$5KBr + KBrO_3 + 6HCl \rightarrow 6KCl + 3H_2O + 3Br_2$$
$$Br_2 + 2KI \rightarrow 2KBr + I_2 \text{: } I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

The materials required are:

$\frac{N}{10}$ solution of potassium bromate-bromide

which consists of a solution of 2·784 grams potassium bromate and 10 grams potassium bromide in one litre of solution.

Other reagents required are:

$\frac{N}{10}$ solution of sodium thiosulphate,

which is 24·83 grams diluted to one litre.

A solution of 125 grams potassium iodide in a litre.

A definite amount of the phenol in aqueous solution, e.g. 25 c.c. containing preferably about 0·1 grams of phenol is run into a glass-stoppered flask. 50 c.c. of bromate-bromide solution is added, followed by 5 c.c. of concentrated hydrochloric acid. The flask is well shaken, and allowed to stand for half an hour; 20 c.c. of potassium iodide solution is added and iodine is liberated. This is titrated with the standard $\frac{N}{10}$ sodium thiosulphate solution using a little starch solution as indicated.

1 c.c. of $\frac{N}{10}$ bromate-bromide solution = 0·001568 grams phenol.

b = c.c. $\frac{N}{10}$ thiosulphate solution

Therefore b c.c. N/10 sodium thiosulphate is equivalent to the same amount of iodine, i.e. the same amount of bromine, and the same no. of c.c. N/10 bromate bromide. So that (50-b) will be the no. of c.c. bromate bromide taken up by the phenol. So the amount of phenol present is determined.

This method is accurate and is also applicable to cresols, xylenols, etc.

Examination of Cresol. Cresol is the leading ingredient of many synthetic resin products. It is a matter of some importance to know which type of cresol is present and particularly how much meta-cresol. The method for considering this aspect is as follows:[7]

10 grams of the sample are weighed into a 50 c.c. Erlenmeyer flask and mixed with 15 c.c. of concentrated sulphuric acid containing 96 parts by weight of pure sulphuric acid and four parts of water. The flask is put in an oven at 100° C. for an hour, and the contents are then transferred to a 1-litre Erlenmeyer flask. This flask is cooled by rotating it for five minutes in a water bath at 20° C., when liquid sulphonic acid will deposit as a thick syrup on the walls of the flask. 90 c.c. of pure nitric acid (density 1·38–1·40 at 15·5° C.) are placed in a 100 c.c. measuring cylinder and about 200 c.c. of this used to dissolve the sulphonic acid in the 50 c.c. flask and then returned to the cylinder. This is repeated till the last trace is removed. Finally, the flask is inverted and drained into the cylinder.

The contents of the cylinder are rapidly transferred to the litre flask and the latter shaken vigorously till all the sulphonic acid is gone and the reaction commences as is shown by the evolution of brown fumes.

The nitration is completed by allowing the flask to stand for 20 minutes, when the contents are poured into a 150 mm. porcelain dish containing 40 c.cs. of water, the flask being rinsed with a further 40 c.c. of water.

The dish and its contents are allowed to stand for two hours, when the solid mass is reduced to a uniform coarse powder by a pestle, and transferred to a Gooch crucible. The apparatus is washed with a wash bottle, using 100 c.c. of water. This is used in such quantities that on transference from the dish to the Gooch crucible, each amount is sufficient only to fill the crucible, which must then be allowed to drain.

When all the powder is in the crucible its contents are dried to constant weight in an oven at 95–100° C. This takes two to three hours.

The trinitrometacresol in the crucible should always remain solid. In the event of liquefaction this indicates the presence of xylenols and the test must be repeated, adding a known weight of pure metacresol to the sample.

The percentage of metacresol in the original sample is easily calculated by multiplying the weight of the trinitrometacresol by the factor 5·714.

Chemical Examination of Phenolic Resins (Cured). (*a*) *Free Phenols.* 5 c.c. of the aqueous extract are added to 10 c.c. of $\frac{N}{10}$ bromide-bromate solution contained in a 100 c.c. stoppered flask. The solution is diluted to 30 c.c. and 5 c.c. of 1 : 1 (by volume) hydrochloric acid added. The mixture is shaken and allowed to stand for half an hour. Then 5 c.c. of 10 per cent aqueous potassium iodide solution are added and the liberated iodine titrated with $\frac{N}{20}$ sodium thiosulphate solution, using starch solution as indicator. A blank is carried out without the aqueous extract, using similar quantities of reagents. The difference in the two titrations, expressed as c.c. of $\frac{N}{20}$ thiosulphate solution, multiplied by 0·16 gives the percentage of phenol in the plastic.

To estimate the amount of ammonia present a small quantity of potassium permanganate solution is added to the aqueous extract and 10 c.c. of aqueous 2 per cent sodium hydroxide. The whole is well mixed, more permanganate being added, if necessary, to maintain the purple colour, and then distilled in an all-glass apparatus. The amount of ammonia is determined colorimetrically with Nessler solution.

(*b*) *Free Formaldehyde.* Free formaldehyde is estimated gravimetrically by means of formaldehyde-dimedone. 100 c.c. of the aqueous extract are used for this test, and 5 c.c. of 5 per cent solution of dimedone in ethyl alcohol are added. The mixture is carefully acidified with dilute hydrochloric acid to the yellow colour of bromo-phenol blue indicator. Dilute sodium hydroxide solution is added until the colour changes to purple, 50 c.c. of a mixture of 2 volumes of $\frac{N}{1}$ sodium acetate and volume of $\frac{N}{1}$ hydrochloric acid are added.

The mixture is allowed to stand for some hours, then filtered, washed free from any chloride with a little cold water and dried to constant weight at 100° C. The percentage of free formaldehyde in the plastic is given by: per cent formaldehyde $= 1{\cdot}03W$, where W is the weight of the formaldehyde-dimedone precipitate.

Nitrogen Estimation. When nitrogen is present, e.g. hexamethylenetetramine, the amount is determined by the Kjeldahl method. The procedure for this is to place about a gram of the powdered sample in a Kjeldahl flask together with 30 c.c. of concentrated sulphuric acid and 10 grams of potassium sulphate. The flask is heated until the solution becomes clear. When cool the solution is diluted with 100 c.c. of water and 50 c.c. of strong sodium hydroxide solution added. Ammonia is given off and distilled into a known amount of $\frac{N}{10}$ sulphuric acid. The excess acid is then titrated with $\frac{N}{10}$ NaOH with methyl orange as indicator. Each 1 c.c. of $\frac{N}{10}$ acid neutralised is equivalent to 0·0014 grams nitrogen.

There are of course a number of products containing furfural or aniline, and these may be expected to increase. They may be recognised along the following lines.

Test for Aniline. A finely ground sample should be boiled for some time with strong aqueous sodium hydroxide, and the liberated aniline extracted with ether. The ether solution is then extracted with HCl. The acid layer is drawn off and warmed to drive off the dissolved ether and then tested with a drop of a hypochlorite. Aniline gives a red-violet colour.

Test for Furfural. Aniline is dissolved in pure glacial acetic acid and added to an acetic acid extract of the powdered resin. If furfural is present a red colour is produced. Quantitative values may be established on a comparative colour basis. Rogers[8] has described a convenient method for estimating furfural.

Amino-Resins. The use of urea-formaldehyde resins has greatly expanded due to their increasing popularity as adhesives, impregnating materials, etc. There is widespread activity in the preparation of solutions of such resins. So that it is desirable to consider some of the leading analytical aspects.

The mouldings are available in all colours and pastel shades. There is no characteristic odour. The main materials are, of course, urea and formaldehyde. However, thiourea is quite extensively used to improve water resistance and moulding characteristics. Comparatively few fillers are employed in urea resins, the most popular, of course, being alpha-cellulose, wood flour, and so on. Solid fillers are comparatively little used. There may be small quantities of catalysts present such as ammonia, hexamethylenetetramine, borax, etc.

The organic fillers are generally best recognised by means of microscopic examination of the solid material. Inorganic fillers are estimated by acting and routine analysis.

The amount of urea present will be determined by straightforward nitrogen determination using the Kjeldahl method. This has already been described. In this instance, 1 c.c. of $\frac{N}{10}$ acid neutralised = 0·003 grams nitrogen.

The purity of urea is estimated on the following lines:

The aqueous solution of urea is diluted with water to an approximate content of 0·1 per cent of urea; 25 c.c. of the solution are treated with 1 gram of potassium bicarbonate and 25 c.c. of $\frac{N}{10}$ bromine in potassium bromide solution, and the mixture is left in a stoppered flask for half an hour. Ten c.c. of 10 per cent potassium iodide solution and about 15 c.c. of N. hydrochloric acid are added, and the liberated iodine is titrated after 15 minutes by $\frac{N}{10}$ sodium thiosulphate solution. A blank determination under the same conditions without the urea solution is carried out at the same time. The difference between the two titrations gives the volume of $\frac{N}{10}$ bromide used up in oxidising the urea. From the equation $CO(NH_2)_2 + 3O \longrightarrow CO_2 + 2H_2O + N_2$, 1 c.c. of $\frac{N}{10}$ bromine is equivalent to 1·00 mg. of urea.

In the preliminary tests with the sample it will be fairly clear whether thiourea is present. The presence of nitrogen and sulphur in the sodium fusion test indicates this.

It is estimated in the following manner: 0·5 grams of the powdered resin is mixed with 10 grams sodium carbonate and 2 grams potassium chloride in a crucible and fused. The melt is cooled, extracted with water, and filtered. The filtrate is made acid with acetic acid, warmed, and barium chloride solution added. Barium sulphate is precipitated, filtered into a Gooch crucible, dried, and weighed. 1 gram barium sulphate is equal to 0·326 grams thiourea.

Analytical Consideration for Cellulose Plastics. Apart from the superficial evidence of such things as the smell of camphor in cellulose nitrate plastics, and the smell of acetic acid in cellulose acetate plastics, some initial tests are required to confirm which type is being considered. The material is ground finely, and a small quantity is heated in an alcoholic solution of potash. The alcohol is evaporated and part of the remainder is heated with dilute sulphuric acid. This will release acetic acid from cellulose acetate or butyric acid from cellulose acetobutyrate. Part of the residue is taken up in water in a test tube. Concentrated sulphuric acid containing a few drops of diphenylamine is carefully added. A dark blue ring where the liquids meet indicates the presence of nitrate.

Cellulose Acetate. Ordinary cellulose acetate is soluble in acetone, but not in chloroform. Cellulose triacetate is soluble in chloroform. This immediately offers a means of separating out the triacetate.

Direct Estimation of Acetyl Content. The behaviour of cellulose acetate depends entirely upon the acetyl content. Acetyl content may be directly determined by saponification. About 1 gram is placed in a 250 c.c. flask fitted with an air condenser; 20 c.c. of pure acetone are added to dissolve the cellulose acetate, followed by 30 c.c. of normal alcoholic potash solution. The mixture is gently boiled for half an hour, cooled, and 50 c.c. of distilled water added in a fine stream with continual swirling. Phenol-phthalein solution is added as indicator and the excess of alkali determined by titration with normal sulphuric acid. A blank determination is carried out at the same time in order to obtain the normality factor for the alcoholic potassium hydroxide solution.

One of the best methods for determining the acetic acid content is first to remove plasticisers by extracting 3 grams with ether.

A preliminary treatment may be required to make it soluble in warm pyridine. The acetone solution of the sample is diluted with 2 to 4 volumes of acetone and poured in a small stream into 6 to 8 volumes of hot water (85° to 95° C.). This gives a finely divided precipitate which dissolves in the pyridine readily.

The residue is then heated at 50° C. for half an hour with 25 ccs. pyridine; 25 c.c. $\frac{N}{2}$ NaOH is added, and heating is continued for another half an hour. The flask is washed with 25 c.c. distilled water. Phenolphthalein is added to act as indicator. Excess alkali is estimated by titration with standard acid solution. This gives a measure of the amount of alkali used which corresponds to the acetyl content of the cellulose acetate.

Free Hydroxyl Content in Cellulose Derivatives. Malm, Genung and Williams[4] have described a method for the determination of free or unsubstituted hydroxyl groups in cellulose derivatives.

One gram of carefully dried material is placed in a 250 c.c. Erlenmeyer flask. 40 c.c. of the special reagent (50 c.c. of acetic anhydride (97 per cent), 950 c.c. of pure, dry pyridine) is added. A blank test is carried out at the same time. The flask heated under reflux for 24 hours at 75–80° C.

After acetylation the excess anhydride is decomposed and the ester precipitated in a soft fine form. In the case of cellulose acetate and other esters of moderate water resistance this can be accomplished by carefully adding water in a fine stream with rapid stirring.

Cellulose acetobutyrate of high butyral content and similar esters of high water resistance must be precipitated by the following method which is generally applicable: Approximately 5 c.c. of distilled water are added through the condenser and mixed by swirling. Heating is continued for a few minutes to complete the decomposition of anhydride. The flask is cooled and removed from the condenser which is then rinsed down with 100–150 c.c. of distilled water, which is caught in a 600 c.c. beaker. The reaction dope, thinned if necessary with pyridine, is poured slowly into the water with vigorous stirring. This precipitate, as specified above, must be soft, fine and easily penetrable otherwise the determination must be repeated.

The solution in the beaker is then titrated electrometrically to a pH value of 9·0. A slightly less sharp and accurate end-point is obtained using phenol-phthalein as indicator. The strength of the reagent is determined by similar treatment of the blank estimations.

The result may be conveniently expressed as per cent of free hydroxyl (equivalent weight 17) as calculated by the equation (c.c. of NaOH for blank – c.c. of NaOH for sample) × NaOH normality × 1·7 divided by the weight of sample taken = per cent free hydroxyl. The free hydroxyl content per unit of glucose in pure raw cellulose is theoretically 31·5 per cent, i.e. three hydroxyl groups per unit of glucose $C_6H_{10}O_5$.

Acetic Anhydride. Acetic anhydride has assumed very considerable commercial importance. It is desirable to have a ready method for estimating the strength. Fleck[2] has described the following method:

The percentage of anhydride cannot be estimated directly, but the following procedure gives accurate results by a combination of two methods.

Procedure. A 2 c.c. sample of the anhydride is run from a burette into a stoppered weighing bottle and weighed accurately. The weighing bottle and contents are then dropped into a 300 c.c. Erlenmeyer flask containing 50 c.c. of normal NaOH and 50 c.c. of water. The flask is shaken to remove the stopper of the weighing bottle, and allowed to stand for about an hour at room temperature with occasional shaking. The mixture is then titrated with normal sulphuric acid, using phenolphthalein as an indicator. From the figure so obtained, the number of c.c. of $\frac{N}{1}$ alkali required to neutralise 100 grams of the hydrolysed acetic anhydride is calculated (A).

About 20 c.c. of perfectly dry, freshly distilled aniline are run into a 50 c.c. weighing bottle and weighed; 2 c.c. of anhydride are then added dropwise from a burette, swirling the contents gently. The bottle is stoppered, allowed to stand at room temperature for an hour, and then weighed again to determine the weight of anhydride added. The contents of the bottle are then washed into a 500 c.c. Erlenmeyer flask with 100 c.c. of 50 per cent neutral alcohol, followed by an additional rinsing with distilled water. The solution is now titrated with $\frac{N}{1}$ alkali. From the result, the number of c.c. of $\frac{N}{1}$ alkali needed to neutralise the acetic acid in 100 grams of the sample is calculated (B).

From equations (i) and (ii)

$$(CH_3CO)_2+H_2O=2\,CH_3COOH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

$$(CH_3CO)_2O+C_6H_5NH_2=C_6H_5N(CH_3CO)H+CH_3COOH \quad . \quad . \quad (ii)$$

the result (A) is therefore a measure of the sum of the acetic acid present as such and of that obtained by hydrolysis. Result (B) is a measure of the sum of the acetic acid present as such and one-half of that present as anhydride. Subtract (B) from (A) to obtain the number of c.c. of normal alkali corresponding to one-half of the acetic anhydride in 100 grams of sample. By multiplying this difference by 0·102, the percentage of anhydride is obtained.

Cellulose Acetobutyrate. Cellulose acetobutyrate and other mixed esters, after having been freed of plasticisers by extraction with carbon tetra-chloride or methanol, should be saponified with N or 0·5 N KOH (5 grams of ester to 100 c.c. of 0·1 N alkali). By refluxing for about 2 hours over a water bath, the alcohol should then be distilled off. The residue is taken up in a little water, the remaining hydrocellulose filtered out, and the filtrate evaporated to dryness over a water bath. The residue should be dissolved in a little water and placed in a fractionating flask (150 to 200 c.c. capacity) with a long arm; 10 c.c. of absolute alcohol and 10 c.c. of concentrated sulphuric acid are then added, and the mixture fractionated in a sand bath. Ethyl acetate distils at 77° C., and ethyl butyrate at 120° C., each recognisable by a characteristic odour.

Cellulose Nitrate. Cellulose nitrate is fairly readily identified as a plastic. For example, it is extremely inflammable. It generally smells strongly of camphor, especially when warmed; it does not withstand high temperature, etc.

The application of cellulose nitrate depends upon its nitrogen content and viscosity. Most cellulose nitrate products have a characteristic yellow-brown fluorescence in ultra-violet light. It may be distinguished from cellulose acetate by its solubility in amyl formate. Cellulose nitrate plastics are generally examined for plasticiser content, camphor content, nitrogen, and ash. The ash content is determined by the usual method of igniting a small amount of the plastic and thereafter subjecting the ash to routine analysis.

Nitrogen Content of Cellulose Nitrate. The following is the usual method adopted for estimating nitrogen in nitro-cellulose.

Camphor and other plasticisers are extracted from the plastic by means of methyl alcohol extraction. It is then dispersed in concentrated sulphuric acid and the nitric acid given off measured in a nitrometer.

The determination is carried out in a Lunge nitrometer provided with a cup and graduated from 100 to 150 c.c. It is filled with mercury and is connected with a compensating tube. The sample is placed in the cup of the nitrometer, and 5 c.c. of pure sulphuric acid 60° Be are added. The material is run into the nitrometer and shaken vigorously. After a short time nitric acid is evolved. The nitrometer is allowed to stand until the acid and mercury have separated. Finally the volume is adjusted to atmospheric pressure, corrected to N.T.P., and the percentage of nitrogen in the sample is determined.

Another method makes use of *nitron.* 1 gram of the cellulose nitrate is saponified with 10 c.c. of 30 per cent NaOH mixed with 1 c.c. of 30 per cent H_2O_2. The mixture is heated over a water bath to 50 or 60° C. Hydrocellulose is precipitated, filtered and washed. Excess hydrogen peroxide is boiled from the filtrate, which is then made mildly acid with acetic acid, and water is added to bring the volume up to 50 c.c. To a fraction of this solution in which there may be 0·01 to

0·05 grams of NO_3 present (in about 5 c.c.), add a few drops of acetic acid, heat to 60° to 70° C., pour in 10 c.c. of 10 per cent nitron acetate solution, and let the mixture stand at room temperature for 24 hours. After decanting as much of the solution as possible, the thin needles of the nitron-nitrate compound ($C_{20}H_{16}N_4.HNO_3$ mol. wt. 375·17) should be filtered out into a filtering crucible which has previously been dried at about 105° C. The precipitate should then be washed with 50 c.c. of saturated nitron-nitrate solution, then taken up with 10–12 c.c. of ice water and the precipitate dried at 100° C., for 2 or 3 hours.

$$\text{Per cent. } HNO_3 = \frac{16{\cdot}798 \times G}{a}$$

where G = the determined amount of nitron-nitrate in grams.
a = the weighed amount of substance used.

Determination of Camphor Content. Two or three grams of the finely divided plastic are refluxed with 150 c.c. of carbon tetrachloride to extract camphor and other plasticisers. The residue, consisting of nitro-cellulose and any mineral fillers, should be dried at about 60° C., and weighed.

Most of the carbon tetrachloride is distilled off over a water bath, and the remainder removed by a steam distillation, which also carries over the camphor. The dry weight of any residue remaining from this steam distillation is determined after removal of water (by distillation) and washing with acetone, and drying. The camphor content (mixed with other substances such as certain plasticisers) is given by the formula $c = a - (b + d)$, where a = the weight of the original plastic sample, b = the weight of the nitro-cellulose plus organic fillers and d = the mixture that remains behind from the steam distillation. The camphor content usually varies from 5 to 30 per cent.

Ethyl cellulose is difficult to identify because it has few distinctive properties. It is unsaponifiable. It has a very wide range of solubility. It is only swelled by ether so that plasticisers can be extracted with ether.

The best test for ethyl cellulose is to identify the ethoxy group: C_2H_5O–. Compounds containing this group form ethyl iodide when heated with hydriodic acid. Ethyl iodide with silver nitrate gives a precipitate of silver iodide.

Test for Ethoxy Group, C_2H_5O–. 10 c.c. of pure hydriodic acid (specific gravity 1·68) are placed in a 50 c.c. flask with about 0·25 grams of finely powdered material. The mixture is boiled in a stream of CO_2 and the evolved vapours are conducted through a reflux condenser (filled with water at 40° to 50° C.) and then through a Geissler tube in which water and 0·2 to 0·5 grams of red phosphorus have been placed. This apparatus is immersed in water at 50° to 60°C. The vapours of ethyl while coming from the apparatus are passed into an Erlenmeyer flask containing aqueous silver nitrate solution and alcohol. A yellow precipitate of silver iodide is formed. The amount of ethoxyl present is determined by the classical Zeisel method.

Polystyrene. In the normal way polystyrene is met with as a transparent, somewhat brittle material An almost certain method of recognition is the unique metallic tinkle polystyrène gives when dropped. Above 300° C. polystyrene breaks down and gives off styrene, which has a typical pungent odour.

Acrylic and Methacrylic Esters. At the present time, of course, methyl methacrylate resin predominates above all others. However, some of the other acrylic resins are beginning to emerge. Methyl methacrylate decomposes when heated above 300° C., and gives off the monomer methyl methacrylate, a clear liquid having a very distinct odour. Plasticisers are used to some extent in moulding powders, and these can be removed by refluxing a finely ground sample with methyl alcohol. The percentage of plasticisers can thus be found. A great deal of information can be obtained by heating a ground sample above 300° C. and collecting the distillate. Methyl methacrylate can be obtained from this by redistilling and collecting the fraction around 100° C., which is the boiling point of methyl methacrylate. Methyl methacrylate can be saponified with alcoholic KOH.

The saponified solution is tested for methanol. This is carried out in the following manner: The portion distilling between 60° and 70° C. is collected. A piece of oxidised copper wire is dipped in. A drop of 0·5 per cent resorcinol solution is then added, followed by concentrated sulphuric acid. A rose red colour at the junction of the two solutions indicates the presence of methanol.

Methanol can be detected as already described.

The saponified solution can be acidified with dilute hydrochloric acid, a little zinc dust added and warmed. The characteristic odour of isobutyric acid indicates methacrylic acid.

Polyvinyl Choride. Analytical work on polyvinyl chloride includes the polyvinyl copolymers, etc. A great deal of work has been carried out in this field, and there is quite a fair amount of information on the subject available. The presence of chlorine will have been shown in the preliminary tests. The initial procedure with compounds based on polyvinyl chloride is to remove the plasticisers, which is carried out by refluxing the material in a Soxhlet apparatus with ether. The solid left in the thimble is thereafter further examined. The make-up of solid material is determined in the usual manner: 2 grams are weighed into a crucible and ignited. The ash is weighed after cooling, and if there are fillers present these can be tested for in the usual manner.

The amount of chlorine present is determined as follows: About a gram of the material is mixed with fusion mixture and fused in a nickel crucible for about an hour. After cooking it is dissolved in boiling water, filtered, and made slightly acid to phenolphthalein. Carbon dioxide is expelled by boiling for a few minutes. The solution is made up to 100 c.c. and the chlorine content is estimated by the Volhard titration method in the presence of nitric acid.

In the case of polyvinyl chloride-acetate copolymer the acetate portion is saponifiable. Thus two grams of finely ground material is refluxed for an hour with alcoholic potash. Of course plasticisers are first removed in the case of compound. The filtrate after the alcoholic potash treatment contains potassium acetate. Acetate is thereafter estimated along conventional lines.

One of the most important analytical aspects of polyvinyl chloride compounds is their thermal stability. This has come to be measured in terms of the time which elapses when a sample is subjected to specific heating conditions before hydrogen chloride is definitely identified. Berger[1] has described the German methods for determining the stability of polyvinyl chloride. One such method consists of drawing off the hydrogen chloride formed through a silvered nitrate solution.

Another more simple method which has come into use is to place 2 grams of the compound at the bottom of a test tube, which is immersed in an oil bath, maintained at a definite temperature, such as 170°C. A piece of Congo red test paper is placed in the test tube. The measure of the stability of the compound is taken as the time elapsing before the indicator paper changes colour from red to blue. This is compared with a known standard.

Estimation of Plasticisers. It has already been pointed out that in many ways plasticisers are every bit as important as the plastic base itself. Consequently it is of great importance to check up on plasticisers as raw materials in the first place. Obviously in the examination of any plastic material information regarding the nature and quantity of the plasticiser is a primary step. They are important as raw materials for the compounder; they are equally important to the consumer in their effects on the performance.

Plasticisers in general are not of much significance in thermosetting plastics. On the other hand they are all-important with thermoplastics. The behaviour of all the cellulose materials, cellulose nitrate, cellulose acetate, ethyl cellulose, etc., is closely bound up with plasticiser content. In the profound expansion of polyvinyl chloride activities plasticiser considerations have probably involved more study than the basic raw materials. The same state of affairs applies to almost all vinyl plastics.

In the preceding analytical discussions one of the first steps in the examination of any plastic has been to remove plasticiser by extraction with ether or methanol or acetone, etc. The following notes relate to some of the more important materials usually encountered.

Preliminary Tests on Extract. In the first place, of course, the solvent which has been employed is distilled off, leaving the plasticiser or mixture of plasticisers together with any other solvent materials.

The residue will generally be of an oily character. It will be found that phthalates of one sort or another are usually present in many plastic compositions, and will therefore be left in this extracted fraction. A small proportion of this plasticiser extract from the plastic material is treated by the following methods to establish whether phthalates are present. Incidentally similar methods can be applied to identify the presence of phthalate in phthalic resins.

One gram of the extract is mixed with 3 grams of phenol, and 3 drops of concentrated sulphuric acid are added. The mixture is heated and forms a dark melted mass. When cooled this is extracted with boiling water dilute and made alkaline with some sodium hydroxide solution. If a phthalate is present, the easily recognised pink colour of phenol phthalein will be evident. Another method is to heat a gram of the extract in a test tube with 2 or 3 grams of resorcinol, heating for 5 minutes. The melt is cooled and extracted with water, diluted, and sodium hydroxide solution added until it is just alkaline. The characteristic greenish fluorescence of fluorescein confirms the presence of phthalate.

The flask and contents are heated under reflux for one hour on the water-bath, the condenser washed with distilled water, and the contents of the flask titrated against $N/_2$ HCl, using phenolphthalein indicator.

A blank should be run on the alcoholic NaOH. The material should contain 98–100 per cent of ester.

Determination of Dibutyl Phthalate. This method is based on the fact that the disodium salt of phthalic acid, which is formed by hydrolysing dibutyl phthalate with alcoholic sodium hydroxide, is insoluble in alcohol.

$$C_6H_4(COO\ C_4H)_2 + 2\ NaOH \rightarrow C_6\ H_4(COO\ Na)_2 + 2\ C_4H_9OH.$$

Method. Approximately 1 gram of the mixture is accurately weighed into a 100 c.c. Pyrex flask; 25 c.c. of ethyl alcohol and 1 gram of NaOH are added; an air condenser is attached (ground glass joints) and the solution boiled gently for 1 hour. During this period, the dibutyl phthalate is hydrolysed and the disodium salt is precipitated in white granular form. The flask is then cooled; 50 c.c. of ethyl alcohol is added through the condenser and the precipitate filtered through a tared No. 4 Jena sintered glass crucible. The precipitate is washed 6 times using approximately 10 c.c. of alcohol each time, placed in an air oven at 105°C. and dried to constant weight. A blank determination is run at the same time.

$$\%\ \text{Dibutyl phthalate} = \frac{(\text{Wt. disod. salt-blank}) \times 100 \times 278}{\text{Wt. of sample} \times 210}$$

The presence of tricresyl phosphate has no influence on this determination.

Tricresyl phosphate is frequently associated with phthalates, and quite often present alone. This will have been identified by ignition of the original material as part of the routine tests on the ash. For example, the extract is treated by hot nitric sulphuric acid mixture. The residual solution is diluted. If phosphate is present, it is readily identified. The final material is diluted and filtered and phosphate is readily recognised by precipitation is ammonium phosphomolybdate. The amount of tricresyl phosphate is determined in the following manner:

Determination of Tricresyl Phosphate. The phosphorus content of tricresyl phosphate can be determined by decomposing the compound and precipitating the phosphoric acid produced as magnesium-ammonium phosphate, which on ignition gives magnesium pyrophosphate.

Method. Approximately 1 gram of the mixture is accurately weighed into a 100 c.c. Pyrex flask; 10 c.c. of concentrated sulphuric acid is added and an air condenser fitted on to the flask (ground glass joints). The mixture is heated gently until thoroughly charred. Concentrated HNO_3 is now poured down the condenser, about 2 c.c. at a time and the mixture warmed after each addition to expel the brown fumes of NO_2. This is repeated until the solution is clear. The condenser is washed with distilled water, and the contents of the flask (approximately 50 c.c.) are washed into a 350 c.c. beaker. Excess magnesia mixture is added and a thin excess of ·88 NH_4OH. The mixture is well stirred and allowed to stand overnight. The precipitate is filtered through a No. 40 Whatman filter paper and washed well with 1 in 20 ammonium hydroxide solution. After drying, the main bulk of the precipitate is removed from the paper, the paper ignited by itself to remove all carbonaceous matter, the main precipitate added, and the whole ignited at bright red heat for 30 minutes. The product is then cooled and weighed as magnesium pyrophosphate.

The theoretical phosphorus content of tricresyl phosphate is 8·42 per cent.

$$\therefore \% \text{ T.C.P.} = \frac{\left(\text{Wt. } Mg_2P_2O_7 \times \frac{62}{222{\cdot}6}\right) \times 100 \times 100}{\text{Wt. of sample} \times 8{\cdot}42}$$

Dibutyl phthalate has been found to have no effect on the determination.

While the aforementioned are the most important plasticisers, there may, of course, be many others present. The examination can be carried further, by saponifying the plasticiser extract with alcoholic potash by refluxing for 2 hours. If phthalate is present, potassium phthalate will have been formed, which is comparatively insoluble in alcohol, and can be filtered off. The bulk of the filter is reduced by evaporation. Dilute hydrochloric acid is added to a portion of this which is warmed. Oil may separate, which is most likely to be castor oil, and in any event is easily recognised.

Lubricating Materials. Many plastics contain lubricating materials in small amounts such as stearic acid, stearates, palmitate, and so on. These are examined in the following manner as raw materials:

Analysis of Calcium Stearate. (i) Free Stearic Acid.—10 grams calcium stearate is weighed into a 250 c.c. flask, and 100 c.c. 1 : 10 HCl. added. The flask is warmed until all the solid is melted, and then cooled with shaking under the tap. Filter in a Buchner funnel, wash with distilled water, keeping the washings. Transfer as much as possible of the precipitate back into the flask, add 50 c.c. of water, warm until solid melts, cool with shaking, and filter. Repeat the last operation. Finally transfer the precipitate of stearic acid to a flask, and wash the filter into the flask with hot alcohol. Dissolve the stearic acid in alcohol, and titrate against N.NaOH, with phenolphthalein indicator. Calculate to stearic acid, subtract the figure for free acid and return as combined acid.

Evaporate the filtrate and washings dry, heating until white. Take up in 200 c.c. 1:4 HCl., heat to boiling for 1 minute, filter, and wash precipitate with hot water. Ignite the precipitate, returning as insoluble matter. Take the filtrate down to 50 c.c., heat to boiling, and make alkaline with ammonia. Filter, wash, ignite precipitate, and return as $Fe_2O_3+Al_2O_3$. Dilute filtrate to 200 c.c., heat to boiling, add 4·5 grams crystalline ammonium oxalate, and make acid with acetic acid. Let the precipitate settle. Wash by decantation, filter, and wash free from chloride. Ignite, and weigh as CaO. The material should contain more than 98 per cent of combined calcium stearate.

Particularly in the case of polyvinyl chloride and copolymer compounds a lead compound is invariable present. White lead is by far the most important material used here. It must be kept under careful control. The following analysis applies to it as a raw material.

Analysis of White Lead. (i) Total Carbonate Content: An absorption train, consisting of soda-lime U—tube, acid flask, reaction vessel, empty flask, concentrated H_2SO_4 flask, anhydrone U-tube, and CO_2 absorption tube (see Treadwell & Hall, p. 344) is set up; 3 grams white lead is weighed into the reaction vessel, and enough distilled water is added to cover the end of the tube from the acid flask; 100 c.c. 2N.HCl is put in the acid flask. The CO_2 absorption tube is weighed, put on to the end of the train, and suction is applied to draw the acid into the reaction vessel. The determination is carried out as in the above reference, the increase in weight of the absorption tube being due to evolved CO_2.

(ii) Total Lead: 1 gram white lead is weighed into a 400 c.c. beaker, and dissolved in dilute HNO_3 by warming. The solution is diluted to 200 c.c., heated to boiling, and dilute H_2SO_4 is added until precipitation is complete. The precipitate of $PbSO_4$ is filtered off, and washed with distilled water, and alcohol. It is dried in the air-oven at 110°C., and the filter paper is incinerated apart from the precipitate in the usual way. The precipitate is added and the whole ignited. Concentrated H_2SO_4 (a few drops) with a little concentrated HNO_3 is added, and ignited. The precipitate is weighed as $PbSO_4$.

REFERENCES

1 BERGER. *Kunstoffe*, 1940, **30**, 357.
2 FLECK. *Plastics*, Temple Press, Ltd., 1944, p. 291.
3 FISCHER. *Laboratoriumsbuch für die organischen Plastischen Kunstmassen*, Knapp, Halle, 1938.
4 MALM, GENUNG AND WILLIAMS, *Ind. Eng. Chem.* (Anal.), 1942, **14**, 935.
5 MARK AND RATH. *High Polymer Reactions*, New York, 1941.
6 NECHEMKIN. *Ind. Eng. Chem.* (Anal.), 1943, **15**, 40.
7 RASCHIG. *Z. angew. Chem.*, 1900, **31**, 759.
8 ROGERS. *Ind. Eng. Chem.* (Anal.), 1944, **16**, 319.

CHAPTER XXXII

THE PHYSICAL TESTING OF PLASTICS

Physical Behaviour of Plastics. While the properties of each group of plastics have been described, there has not been any effort at comparing their characteristics, yet it is precisely the physical properties which are of outstanding importance for most practical applications. As the uses of plastics spread throughout engineering industries so the mechanical characteristics assume greater importance.

It is extremely interesting to study briefly the methods generally employed to evaluate these properties. It then becomes possible to select the best type of material for any field of application. There is no doubt that much more accurate information on mechanical properties is essential. As Livingston Smith[8] has pointed out: "If the engineer is to consider the use of plastics in stressed parts he will require more complete and certainly more accurate mechanical data than are at present generally available. The behaviour under stress of all plastic materials is very different from that of metal, as will be understood when it is recalled that their structure consists of long chains held together by secondary forces as compared with the crystalline structure of metals. This difference is reflected in the methods necessary to secure accurate test data. Thus, plastics seldom exhibit a marked yield point; they tend to creep at normal temperatures, and they fail to obey Hooke's Law precisely.

"In testing plastics, one must also bear in mind the effect of moisture content and temperature. Great care is necessary to subject test pieces to a standard conditioning treatment before test. It is also necessary, if the test is to occupy any length of time, to arrange for constant conditions of temperature and humidity in the testing laboratory."

In Great Britain most testing is carried out along lines laid down by the British Standards Institution. It is a most unfortunate circumstance that very few standards have so far been set up relating directly to plastics. Indeed, only one publication, B.S.S. 771/1948, is directly concerned with detailed testing of plastic moulding materials—even this is confined in its scope to phenol formaldehyde resins. Nevertheless, this is used freely for almost every type of rigid plastic.

For those materials having rubber-like properties, the tests which are usually applied are those which the British Standards Institution has evolved for testing rubber. A very comprehensive series of tests are laid down in B.B.S. 903/1940.

In regard to specifications for testing, it must be admitted we are far behind the United States. The American Society for Testing Materials already has a wide range of test methods defined specifically for plastics.

In the tables which are given in a subsequent discussion, it must be remembered that figures merely give the limits which can be expected from the commercial range of materials. The compositions based on each plastic, can, with one or two exceptions be subject to infinite variations of resin content, plasticiser content, filler content, and so on. Therefore, unless a specific composition is selected in each instance, it is only possible to give properties within wide limits.

The Flowing Characteristics of Plastics. The flow of plastics is clearly a matter of primary importance, more particularly for moulding activities. In this country the Cup Flow Test is standardised for testing the behaviour of phenolic moulding powders. The conditions under which it is carried out are defined in B.S.S. 771/1948.

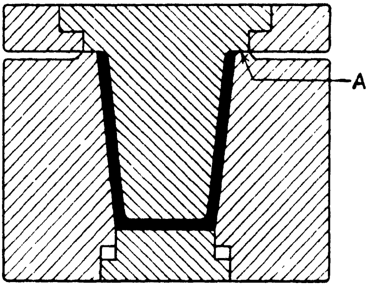


Fig. 254. Arrangement for cup-flow test. A is the "flash"

The Cup Flow Test. A test cup is moulded in a mould of specified dimensions under fixed conditions. The time of flow is measured in seconds by means of a stop-watch and is taken as the time in seconds from the instant the hydraulic gauge shows pressure to the instant the flash ceases to move. A fully moulded cup or beaker is obtained with a base of varying thickness.

The temperature of the mould is 163° C., and a pressure of 10 tons is applied to the mould. The weight of powder employed is sufficient to give a flash of between 2 to 3 grams. The powder at room temperature is placed in the mould, and the mould is closed, which should take between 5 and 10 seconds.

The results are given as the number of seconds flow by the cup flow test. Commercial materials give results between 4 and 30 seconds.

The cup flow test can be criticised on a number of grounds. Nevertheless, it is a test carried out under actual moulding conditions, and by and large has been found very successful.

The cup flow method has not proved to be satisfactory in the case of urea-formaldehyde moulding powders. The best method appears to be to press a definite quantity of the powder under specified temperature and pressure conditions without any confining mould. A disc is formed and the diameter of the disc gives a measure of the relative flow.

The Rossi-Peakes Method. In the United States, the American Society for Testing Materials has adopted the Rossi-Peakes flow tester as the basis for their standard method. The Rossi-Peakes apparatus enables the determination not only of the comparative plastic flow but also the time of cure. It is admirably suited both for thermosetting and thermoplastic materials.

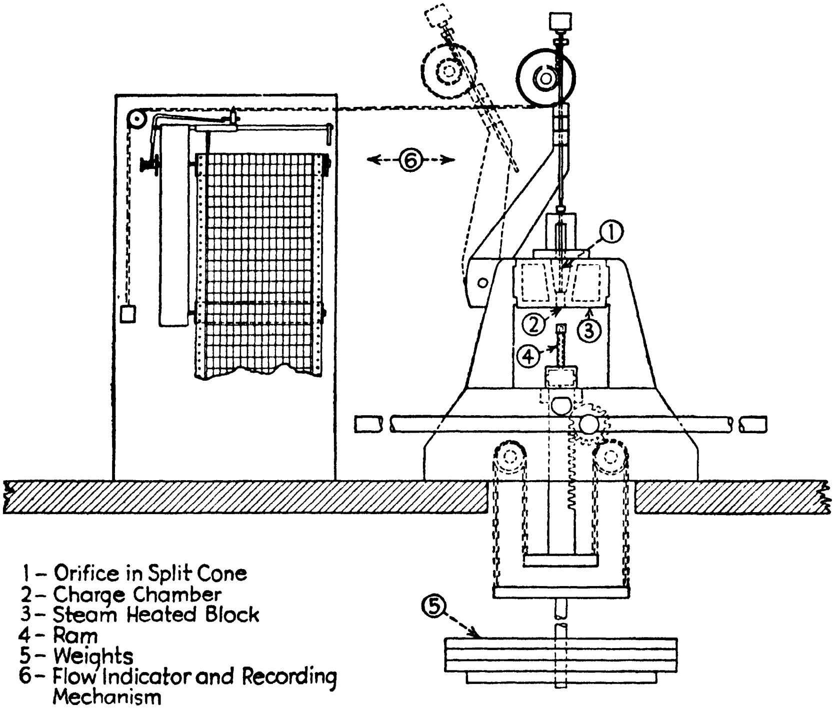


Fig. 255. Diagrammatic sketch of Rossi-Peakes flow tester

A diagrammatic cross section of this machine is shown in Fig. 255. The test pellet, preformed into a cylinder ·375 in. in diameter by ·33 in. high and weighing ·645 grams, is placed on the plunger (4) which carries it into cavity (2) and exerts a pressure on it depending upon the weight (5) applied. The cavity is maintained at a constant temperature by a steam jacket through which high-pressure steam is passed. When the plastic pellet softens, the pressure forces it to flow through the channel in a split cone. A pin is thereby forced up and the distance of its travel, i.e. the distance of plastic flow, is recorded on a graph paper which is wound over rolls by an automatic timing device. The rate of flow is thus automatically plotted. Plastic flow ceases when the plastic is cured, and this is recorded.

In the case of themoplastic materials a moulded or machined test piece 0·375 inches in diameter by 0·375 inches high is employed. In this case the distance through which the pin is pushed in a definite time, e.g. 2 minutes, is measured. Each material is tested at three or more temperatures at which the flow will be between 0·5 to 1·5 inches, with at least one measurement above and below 1 inch. The flow is then plotted on semi-logarithmic paper usually giving a straight line. The temperature at which flow is exactly 1 inch is read off and is taken as the flow temperature. It has recently been discussed by Pilch and Gloor.[9]

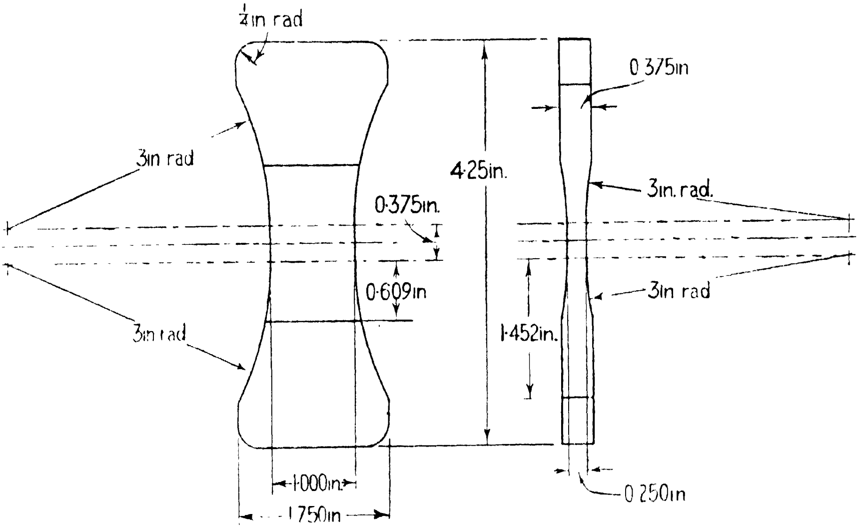


Fig. 256. Test piece for rigid plastics

Tensile Tests on Plastics. Tensile strength is the load per unit area required to break the material under test. Tensile tests on plastics really divide into two well defined categories, the one applies to rigid plastics with comparatively small elongations while the other applies to soft extensible materials which may have high elongations comparable to that of rubber. In a sense we come back to the division between soft rubber compositions—ebonite. Tests for these have been the subject of much study. They are applied to plastics. Suitable methods are outlined in B.S.S. 903/1940 and B.S.S. 771/1948.

Rigid Materials. According to B.S.S. 771, a specimen of the plastic material whether thermosetting or thermoplastic, is moulded to the shape and dimensions illustrated in Fig. 256. The test piece is held in special grips which prevent it from slipping, being mounted in standard tensile machines. The load is applied, and the load and elongation at break are noted. The ultimate tensile strength is calculated from the dimensions of the specimen.

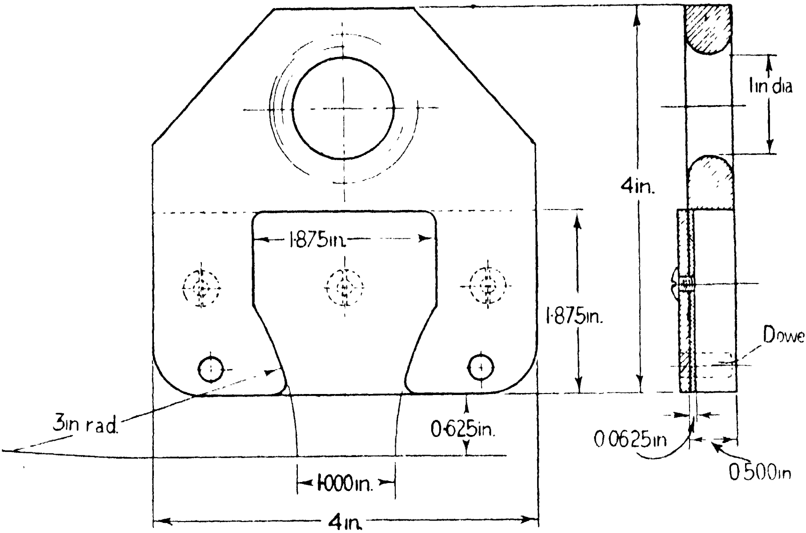


Fig. 257. Holder for rigid tensile test piece

Extensible Materials. The practice here corresponds very closely to that employed for rubber. Dumb-bell shaped test pieces are more usually employed. Sheets of the material to be tested are prepared and dumb-bells are cut out by punching with a suitable die. A definite length, i.e. 1 inch is marked on the narrow centre portion. The stress as it stretches, is recorded.

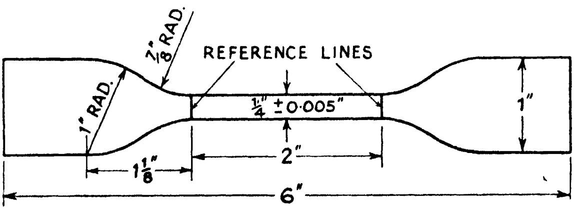


Fig. 258. Test piece for tensile tests

B.S.S. 903 gives the desired conditions applying to rubber which are quite generally used for extensible plastics. The thickness of test piece is usually less than 3 millimetres and is carefully checked by micrometer readings.

Tensile machines most widely used types are the Scott testing machine and the Schopper testing machine. The dumb-bells are beld in grips which exert a uniform pressure on the test piece. The jaws of the testing machine separate at a uniform rate generally 18 inches per minute. Modern tensile machines automatically record the loads and elongations. It is customary to take the average of results on four test samples. The values obtained by extending the test samples are plotted and give characteristic stress-strain curves.

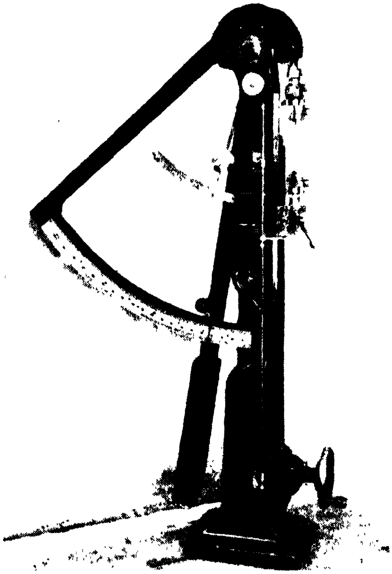


Fig. 259. Typical semi-automatic tensile testing machine

Elongation at break is a matter of some significance in rubber-like plastics, many of which have high elongation at break, equal to rubber compounds, Leading types include polyvinyl chloride, copolymer acrylic resins, polyvinyl butyral and so on. Elongation is also a matter of profound practical significance for nitro-cellulose plastics, and polyamides.

Perhaps more important still is the permanent deformation obtained when plastics are subjected to slow stretching. Rubber mixes have good recovery showing very low permanent deformation.

In the case of thermoplastics, however, the permanent elongation or deformation is generally quite considerable, depending on the duration of the preliminary stretching, a gradual flow of the stretched material being observed already at ordinary temperatures during the stretching. In other words that is pronounced deformation. If in practical use a material be subjected to prolonged mechanical stress, thermoplastics as a rule show the stronger tendency to alter in shape, they are inferior to rubber in this respect.

TABLE 173

TENSILE STRENGTH OF PLASTICS

Material	lb./in.^{2}
Phenol-formaldehyde (no filler)	6,000– 9,000
Phenol-formaldehyde (wood flour filler)	4,000–11,000
Phenol-formaldehyde (mineral filler)	4,000–10,000
Phenol-formaldehyde (fabric filler)	6,500– 8,000
Phenol-formaldehyde (paper laminated	7,000–19,000
Phenol-formaldehyde (fabric laminated)	7,000–16,000
Phenol-formaldehyde (asbestos laminated)	7,000–18,000
Phenol-formaldehyde (cast)	5,000–12,000
Phenol-formaldehyde (glass fabric laminated)	14,000–20,000
Phenol-furfural (wood flour filler)	6,000–11,000
Urea-formaldehyde (moulded)	9,000–12,000
Melamine (filled)	6,000–10,000
Cellulose acetate (sheet)	5,000–11,000
Cellulose acetate (moulded)	2,000–10,000
Cellulose acetobutyrate	3,500– 7,000
Cellulose nitrate	5,000–10,000
Ethyl cellulose	6,000– 9,000
Polystyrene	5,000– 8,000
Polythene	1,200– 1,700 (15,000 drawn)
Polyvinyl chloride (plasticised)	1,000– 9,000
Polyvinyl chloride-acetate (no filler)	8,000–10,000
Polyvinyl chloride-acetate (filled)	6,000–12,000
Polyvinyl formal	3,000–14,000
Polyvinyl butyral	2,500– 8,000
Polyvinyl alcohol	2,000– 5,000
Polyvinylidene chloride	5,000–12,000 (40,000 drawn)
Methyl methacrylate (cast)	7,000– 9,000
Methyl methacrylate (moulded)	4,000–11,000
Nylon	5,000– 9,000 (60,000 drawn)
Casein	7,500

Compressive Strength. Compressive strength is generally carried out on a cylinder of material. In B.S.S. 903 for ebonite, which is a proof test, the dimensions recommended are 12 millimetres diameter and 12 millimetres long. Here the test piece is placed on a flat surface, an initial load of 100 kilograms imposed, and the load is gradually increased so as to reach the maximum rapidly. In the case of ebonite the specification load must be reached in a minute and the test piece must withstand this load for a further minute without crushing. To find the absolute compressive strength, the loading is carried forward until the sample is crushed under the load. Similar tests may be carried out on every type of plastics material.

In Relation to Laminated Materials. B.S.S. 972 calls for a proof compression test on a 1-inch cube of material. A bedding-down load of 300 lb. is applied perpendicular to the laminations, followed by a proof load of 10,000 lb. The deflexion consequent on the application of this proof load is not to exceed 0·04 inch.

TABLE 174

COMPRESSIVE STRENGTH OF PLASTICS

Material	lb/in.^{2}
Phenol-formaldehyde (no filler)	
Phenol-formaldehyde (wood flour filler)	16,000–36,000
Phenol-formaldehyde (mineral filler)	18,000–36,000
Phenol-formaldehyde (fabric filler)	20,000–30,000
Phenol-formaldehyde (paper laminated)	20,000–40,000
Phenol-formaldehyde (fabric laminated)	20,000–44,000
Phenol-formaldehyde (asbestos laminated)	18,000–45,000
Phenol-formaldehyde (cast)	15,000–30,000
Phenol-formaldehyde (glass fabric laminted)	40,000–50,000
Phenol-furfural (wood flour filler)	28,000–36,000
Urea-formaldehyde (moulded)	24,000–35,000
Melamine (filled)	
Cellulose acetate (sheet)	4,000–16,000
Cellulose-acetate (moulded)	11,000–28,000
Cellulose-acetobutyrate	11,000–21,000
Cellulose nitrate	20,000–30,000
Ethyl cellulose	10,000–12,000
Polystyrene	6,500–18,000
Polythene	
Polyvinyl chloride (plasticised)	
Polyvinyl chloride-acetate (no filler)	10,000–12,000
Polyvinyl chloride-acetate (filled)	
Polyvinyl formal	
Polyvinyl butyral	
Polyvinyl alcohol	
Polyvinylidene chloride	9,000–10,000
Methyl methacrylate (cast)	10,000–15,000
Methyl methacrylate (moulded)	
Nylon	
Casein	3,000–6,000

When tests on cubes are carried to destruction, failure usually takes the form of shearing on planes inclined at 45 degrees to the laminations.

Impact Resistance of Plastics. The impact resistance or toughness of plastics material is a matter of great importance. It may be defined as the energy of the blow required to fracture a bar-shaped test piece of given dimensions held as a cantilever and struck at the free end. The behaviour of materials to sudden blows or shocks is clearly a primary characteristic. Service failure of material even occurs by sudden impact. A great deal of work has been done to study the behaviour of materials under such circumstances.

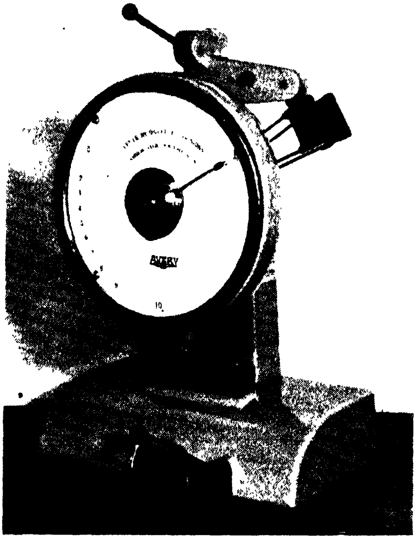


Fig. 260. Typical Avery impact testing machine using the Izod method. There is a gripping device for the test piece; the pendulum has a convenient release; the indicator gives direct reading in ft. lb.

Two methods predominate for determining the impact strength of materials; they are the Izod method and the Charpy method. The first method is widely used in this country, while the Charpy method appears to be favoured in the United States. Both are based on pendulum machines, that is to say, a standard specimen of material is broken by a single blow of a heavy calibrated pendulum. The energy absorbed in breaking the material is calculated from the difference between the initial position of the pendulum and the height which it reaches after breaking the specimen.

TABLE 175

MODULUS OF ELASTICITY OF PLASTICS

Material	Modulus of Elasticity (lb./sq. in. × 10^5)
Phenol-formaldehyde (no filler)	7·0–10·0
Phenol-formaldehyde (wood flour filler)	10·0–10·0
Phenol-formaldehyde (mineral filler)	10·0–15·0
Phenol-formaldehyde (scrap fabric filler)	7·0–12·0
Phenol-formaldehyde (paper laminated)	4·0–20·0
Phenol-formaldehyde (fabric laminated)	3·5–15·0
Phenol-formaldehyde (asbestos laminated)	3·5–15·0
Phenol-formaldehyde (cast)	5·0–15·0
Phenol-formaldehyde (glass fabric laminated)	10 –20
Phenol-furfural (wood flour filler)	10·0–25·0
Urea-formaldehyde (moulded)	4·6– 5·1
Melamine (filled)	12 –15
Cellulose acetate (sheet)	1·0– 1·3
Cellulose acetate (moulded)	1·0– 4·0
Cellulose acetobutyrate	2·0– 3·5
Cellulose nitrate	2·0– 4·0
Ethyl cellulose	2·0– 4·0
Polystyrene	12·0–15·0
Polythene	
Polyvinyl chloride (plasticised)	5·0
Polyvinyl chloride-acetate (no filler)	3·5– 4·0
Polyvinyl chloride-acetate (filled)	3·5– 8·5
Polyvinyl formal	
Polyvinyl butyral	
Polyvinyl alcohol	
Polyvinylidene chloride	0·8 –1·7
Methyl methacrylate (cast)	4·0 –6·0
Methyl methacrylate (moulded)	6·0
Nylon	4·5
Casein	5·1 –5·7

The Izod Test. The Izod test is carried out on a cantilever basis. A specially prepared rod of the material is supported at one end vertically in the plane in which the pendulum is moving. The test bar may be plain or notched. Particulars of the conditions for this test are described in B.S.S. 903.

For the Izod Test, a moulded bar 2·5 inches long by 0·5 inches wide and 0·5 inches thick has a V-shaped notch cut in, 1·25 inches along the bar, to a depth of 0·1 inches. It is clamped at the notch and then struck by the pendulum falling from a height of one foot.

The Charpy Test. In this instance the rod of material, notched or plain, is supported at both ends. It is struck in the middle by the swinging falling pendulum.

In both these methods it is not easy to obtain very accurate results. However, among groups of materials the results show a different order of behaviour which gives ample information regarding the relative impact strength.

TABLE 176

IMPACT STRENGTH OF PLASTICS

Material	Impact Strength (ft./lb. to break) ½″ × ½″ bar
Phenol-formaldehyde (no filler)	·16– ·20
Phenol-formaldehyde (wood flour filler)	·20– ·40
Phenol-formaldehyde (mineral filler)	·11– ·36
Phenol-formaldehyde (scrap fabric filler)	·4 –2·3
Phenol-formaldehyde (paper laminated)	·3 –3·80
Phenol-formaldehyde (fabric laminated)	·8 –8·0
Phenol-formaldehyde (asbestos laminated)	·9 –5·5
Phenol-formaldehyde (cast)	·10–0·50
Phenol-formaldehyde (glass fabric laminated)	5 –6·5
Phenol-furfural (wood flour filler)	0·3 – ·6
Urea-formaldehyde (moulded)	·14– ·16
Melamine (filled)	0·3 –0·4
Cellulose acetate (sheet)	0·75– ·6
Cellulose acetate (moulded)	0·5 – ·5
Cellulose acetobutyrate	0·7 – ·6
Cellulose nitrate	2 – ·8
Ethyl cellulose	0·5 – ·6
Polystyrene	·20– ·50
Polythene	3
Polyvinyl chloride (plasticised)	—
Polyvinyl chloride-acetate (no filler)	·30– ·60
Polyvinyl chloride-acetate (filled)	·10– ·70
Polyvinyl formal	·3 – ·7
Polyvinyl butyral	—
Polyvinyl alcohol	—
Polyvinylidene chloride	1–4
Methyl methacrylate (cast)	·20– ·40
Methyl methacrylate (moulded)	·20– ·40
Nylon	0·9
Casein	1·00

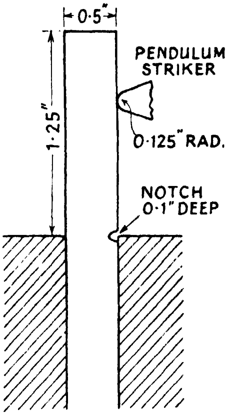


Fig. 261. Set-up for Izod test

Impact strength together with tensile strength is generally taken as an indication of the toughness of materials. These properties are really inadequate to define toughness. It is a property which depends to some extent on the ability of the material to elongate and flex without permanent deformation. But other factors are also involved, and the problem of a test method has not been solved. Thus cellulose plastics are outstanding in their toughness and ability to withstand abuse. As there are no figures for expressing toughness, comparisons between the different materials will have to depend on practical experience based on use. Polyvinyl copolymer plastics probably come nearest to the cellulose plastics in toughness. At the lower end of the scale are the ordinary thermosetting mouldings, and polystyrene.

Flexural Strength of Plastics. The flexural strength of plastic materials is a matter of considerable importance. It gives an indication of the elastic characteristics. It requires even greater significance as plastics begin to enter the field of structure-bearing materials. One of the methods employed for determining the flexural strength is that developed by the A.S.T.M. Standard D. 48–33. A standard bar 5 inches long by ½ inch by ½ inch is moulded and placed on supports 4 inches apart. A load is applied half-way between the supports. The bar will bend as the load is increased, and the distance through which the bar bends before it breaks is called the deflection. The load required to break the bar is expressed as the flexural strength of the material concerned.

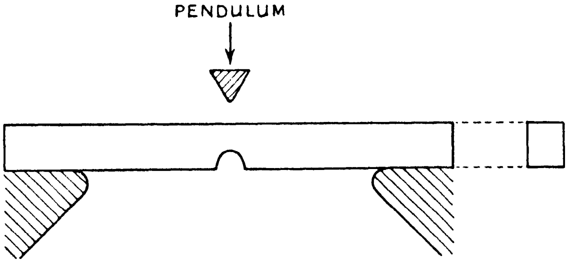


Fig. 262. Set-up for Charpy test

A number of factors have a pronounced influence on flexural characteristics; for example, the binding material, as in the case of phenol formaldehyde resin, fillers, and so on.

TABLE 177

FLEXURAL STRENGTH OF PLASTICS

Material	Flexural Strength lb./sq. in.
Phenol-formaldehyde (no filler)	12,000–17,000
Phenol-formaldehyde (wood flour filler)	8,000–15,000
Phenol-formaldehyde (mineral filler)	8,000–20,000
Phenol-formaldehyde (scrap fabric filler)	10,000–13,000
Phenol-formaldehyde (paper laminated)	13,000–30,000
Phenol-formaldehyde (fabric laminated)	13,000–30,000
Phenol-formaldehyde (asbestos laminated)	10,000–35,000
Phenol-formaldehyde (cast)	—
Phenol-formaldehyde (glass fabric laminated)	20,000–30,000
Phenol-furfural (wood flour filler)	8,000–15,000
Urea-formaldehyde (moulded)	10,000–13,000
Melamine (filled)	9,000–10,000
Cellulose acetate (sheet)	—
Cellulose acetate (moulded)	2,000–16,000
Cellulose acetobutyrate	5,500–12,000
Cellulose nitrate	8,000–10,000
Ethyl cellulose	9,000–10,000
Polystyrene	14,000–19,000
Polythene	—
Polyvinyl chloride (plasticised)	—
Polyvinyl chloride-acetate (no filler)	10,000–13,000
Polyvinyl chloride-acetate (filled)	7,500–12,000
Polyvinyl formal	—
Polyvinyl butyral	—
Polyvinyl alcohol	—
Polyvinylidene chloride	15,000–17,000
Methyl methacrylate (cast)	14,000
Methyl methacrylate (moulded)	10,000–15,000
Nylon	10,000–15,000
Casein	10,000–18,000

Volume Resistivity and Surface Resistivity. Surface resistivity is the electrical resistance on the surface of a material between the opposite sides of a one-centimetre square. It therefore indicates the amount of current which is enabled to pass over the surface of a material or the leakage. According to B.S. 771 applying to phenolic moulding materials and to B.S. 903 which applies to rubber compounds, a moulded disc between 4 inches and 5 inches diameter is first conditioned by immersion in water for 24 hours at an ordinary temperature. It is then dried between blotting-paper and tested.

The specimen is placed in a trough. A copper ring or tube with knife edges is superimposed on the test specimen. Within this ring or tube a layer of mercury is poured. A space of 1 centimetre wide is left outisde this ring and then 2 more tubes with sharp edges are set up half a centimetre apart, and a layer of mercury is poured into this ring. In this manner there is an outer ring of mercury in contact with the specimen, a clear area of specimen, and a disc of mercury in contact with the specimen. The inner mercury is connected with the positive end of the d.c. current line. The outer ring of mercury is connected to the galvonometer and the negative end of the line. The sample is subjected to electrification of 500 volts for one minute. The resistance of the circuit is measured. The surface resistivity is then calculated from the formula.

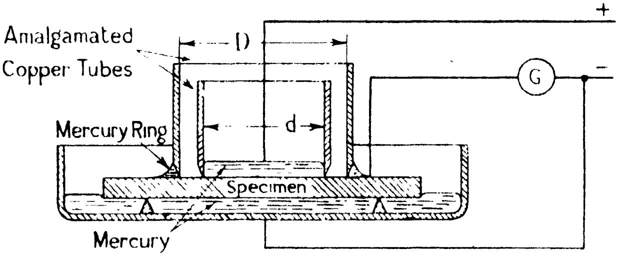


Fig. 263. Electrical connections for surface resistivity test

$$S = \frac{2\pi R}{\log_e \frac{D}{d}}$$

where S = Surface resistivity (in megohms)
R = Surface resistance (in megohms)
D = Internal diameter of exterior tube (cm.)
d = Internal diameter of interior tube (cm.)

While surface resistivity or leakage is sometimes of great importance, the more usual determination is the volume resistivity which is carried out with a similar set-up of apparatus as described for surface resistivity. The only difference is in the connections of the circuit which are not the same. The volume resistance of the test piece is measured at a potential difference of 500 volts d.c., after 1, 2, or 10 minutes electrification. The volume resistivity is then calculated from the following formula:

$$V = \frac{\pi d^2 R}{4T}$$

V = Volume resistivity (megohm. cm.)
R = Volume resistance (megohms)
d = Internal diameter of interior tube in cms.
T = Thickness of test piece in cms.

TABLE 178

VOLUME RESISTIVITY OF PLASTICS

Material	Volume Resistivity ohms-cm.[3])
Phenol-formaldehyde (no filler)	$1{\cdot}0 \times 10^{12}$–$5{\cdot}0 \times 10^{12}$
Phenol-formaldehyde (wood flour filler)	10^{10}–10^{12}
Phenol-formaldehyde (mineral filler)	10^{9}–10^{11}
Phenol-formaldehyde (scrap fabric filler)	10^{9}–10^{11}
Phenol-formaldehyde (paper laminated)	10^{10}–10^{13}
Phenol-formaldehyde (fabric laminated)	10^{10}–10^{12}
Phenol-formaldehyde (asbestos laminated)	—
Phenol-formaldehyde (cast)	10^{9}–10^{14}
Phenol-formaldehyde (glass fabric laminated)	—
Phenol-furfural (wood flour filler)	10^{10}–10^{12}
Urea-formaldehyde (moulded)	$2{\cdot}0 \times 10^{13}$–$2{\cdot}8 \times 10^{13}$
Melamine (filled)	5×10^{11}
Cellulose acetate (sheet)	$5{\cdot}0 \times 10^{12}$–$30{\cdot}0 \times 10^{12}$
Cellulose acetate (moulded)	10^{10}–10^{12}
Cellulose acetobutyrate	10^{12}
Cellulose nitrate	$2{\cdot}0 \times 10^{10}$–$30{\cdot}0 \times 10^{10}$
Ethyl cellulose	10^{15}
Polystyrene	10^{17}
Polythene	10^{17}
Polyvinyl chloride (plasticised)	Up to 10^{14}
Polyvinyl chloride-acetate (no filler)	10^{14}
Polyvinyl chloride-acetate (filled)	Up to 10^{14}
Polyvinyl formal	10^{15}
Polyvinyl butyral	Up to 10^{14}
Polyvinyl alcohol	—
Polyvinylidene chloride	10^{15}
Methyl methacrylate (cast)	10^{15}
Methyl methacrylate (moulded)	10^{15}
Nylon	10^{13}
Casein	—

Water Absorption. The amount of water absorbed by a plastic may be of significance in a number of uses. It particularly affects the electrical characteristics, it may completely spoil transparency, it may influence adhesion and so on.

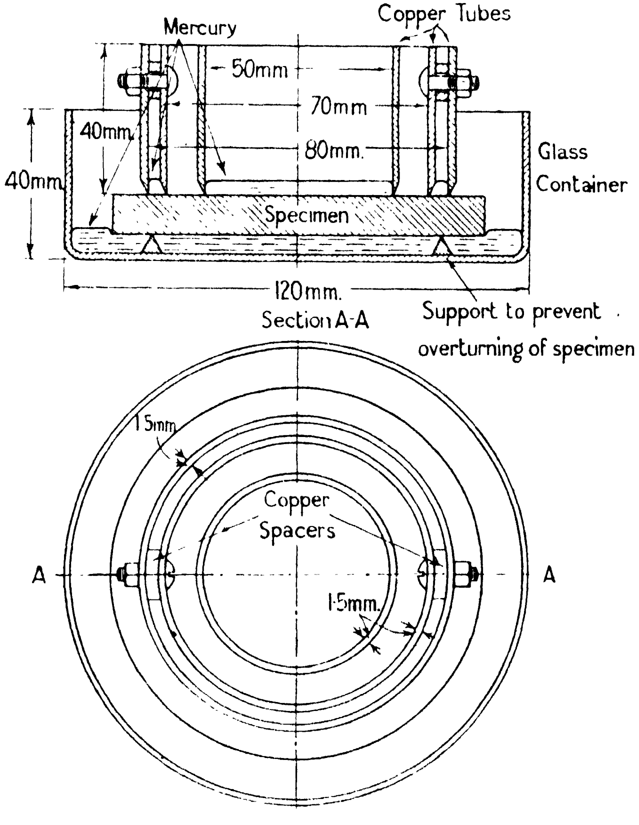


Fig. 264. Set-up for surface resistivity tests

The procedure adopted to determine water absorption varies. In some cases water absorption is determined after direct immersion in water at a considerable temperature, the sample being weighed before and after immersion. For comparative tests the size of the samples would be identical. In some instances the water absorption at a definite degree of humidity is preferred.

In the case of plasticiser materials, the direct values obtained in this manner are not accurate since there is a tendency for plasticiser to be leached out. This applies particularly to cellulose acetate plastics, etc.

B.S.S. 771 describes a test for moulded materials. A disc 50 mm. diameter by 12 mm. thick is dried at 50°C. for one hour and weighed. It is then immersed for 165–170 hours in water at 20°C. The surfaces are then dried with blotting paper and the sample re-weighed. The water absorption may be expressed in milligrams or as a percentage.

TABLE 179

WATER ABSORPTION OF PLASTICS (24 HOURS' IMMERSION)

Material	Water Absorption %
Phenol-formaldehyde (no filler)	·10– ·20
Phenol-formaldehyde (wood flour filler)	·20– ·60
Phenol-formaldehyde (mineral filler)	·01– ·30
Phenol-formaldehyde (scrap fabric filler)	1·00–1·30
Phenol-formaldehyde (paper laminated)	·30–9·00
Phenol-formaldehyde (fabric laminated)	·30–9·00
Phenol-formaldehyde (asbestos laminated)	·30–2·00
Phenol-formaldehyde (cast)	·01– ·50
Phenol-formaldehyde (glass fabric laminated)	0·3 –0·5
Phenol-furfural (wood flour filler)	·20– ·60
Urea-formaldehyde (moulded)	1·00–2·00
Melamine (filled)	·15– ·3
Cellulose acetate (sheet)	1·5 –3·0
Cellulose acetate (moulded)	1·4 –2·8
Cellulose acetobutyrate	·80–1·10
Cellulose nitrate	1·00–3·00
Ethyl cellulose	1·25
Polystyrene	nil
Polythene	nil
Polyvinyl chloride (plasticised)	0·5
Polyvinyl chloride-acetate (no filler)	·03– ·15
Polyvinyl chloride-acetate (filled)	·20–4·00
Polyvinyl formal	1·3
Polyvinyl butyral	3·5 –4·5
Polyvinyl alcohol	—
Polyvinylidene chloride	nil
Methyl methacrylate (cast)	·40
Methyl methacrylate (moulded)	·40– ·50
Nylon	Up to 7·6
Casein	7·0 –9·0

Electrical Breakdown Strength. Electrical breakdown strength or dielectric strength is the electric stress required to produce a disruptive charge through the material. It will vary with the thickness of the test piece, e.g. dielectric strength of films will be greater per unit of thickness than in the case of thicker sections.

According to British Standards Specification (B.S.S. 903), this is carried out on a 4 inch disc 0·125 inch thick. The test pieces are subjected to 48 hours conditioning in an atmosphere of 75 per cent relative humidity at 22°C.

TABLE 180

BREAKDOWN VOLTAGE AT 50 CYCLES FOR PLASTICS

Material	Breakdown Voltage volts/mil.-instantaneous	Long Term
Phenol-formaldehyde (no filler)	400– 500	
Phenol-formaldehyde (wood flour filler)	300– 500	200–400
Phenol-formaldehyde (mineral filler)	250– 400	200–400
Phenol-formaldehyde (scrap fabric filler)	150– 450	100–350
Phenol-formaldehyde (paper laminated)	400–1,200	250–600
Phenol-formaldehyde (fabric laminated)	250– 450	100–350
Phenol-formaldehyde (asbestos laminated)	60– 150	50–125
Phenol-formaldehyde (cast)	300– 450	250–350
Phenol-formaldehyde (glass fabric laminated)	450– 650	—
Phenol-furfural (wood flour filler)	400– 600	
Urea-formaldehyde (moulded)	650– 720	
Melamine (filled	400	350
Cellulose acetate (sheet)	600–1,000	
Cellulose acetate (moulded)	300– 600	200–300
Cellulose acetobutyrate	250– 400	—
Cellulose nitrate	600–1,200	
Ethyl cellulose	1,500	—
Polystyrene	500– 700	450–600
Polythene	1,000	—
Polyvinyl chloride (plasticised)	600–2,000	
Polyvinyl chloride-acetate (no filler)	600	
Polyvinyl chloride-acetate (filled)	650	
Polyvinyl formal	700	500
Polyvinyl butyral	300– 400	300
Polyvinyl alcohol	—	—
Polyvinylidene chloride	500–2,000	—
Methyl methacrylate (cast)	500	
Methyl methacrylate (moulded)	500	
Nylon	500	350
Casein	400– 700	

TABLE 181—DIELECTRIC CONSTANTS FOR PLASTICS

Material	Dielectric Constant			Radio Frequencies
	@ 50 cycles	@ 10^3 cycles	@ 10^6 cycles	
Phenol-formaldehyde (no filler)	5·0–6·0	4·0–5·0	4·5–5·0	4·5–7·0
Phenol-formaldehyde (wood flour filler)	5·0–12·0	4·0–8·0	4·5–8·0	4·5–8.0
Phenol-formaldehyde (mineral filler)	5·0–20·0	4·5–20·0	4·5–20·0	4·5–20·0
Phenol-formaldehyde (scrap fabric filler)	5·0–10·0	4·5–6·0	4·5–6·0	4·5–7·0
Phenol-formaldehyde (paper laminated)	—	—	3·6–5·5	4·5–8·0
Phenol-formaldehyde (fabric laminated)	—	—	4·5–7·0	4·5–7·0
Phenol-formaldehyde (asbestos laminated)	—	—	—	—
Phenol-formaldehyde (cast)	5·0–10·0	—	5·0–8·0	4·5–7·0
Phenol-formaldehyde (glass fabric laminated)	—	—	—	—
Phenol-furfural (wood flour filler)	—	4·0–8·0	6·0–7·5	—
Urea-formaldehyde (moulded)	—	—	—	—
Melamine (filled)	6·5–10·0	—	7·0	—
Cellulose acetate (sheet)	3·5–7·5	3·5–7·0	3·0–5·0	—
Cellulose acetate (moulded)	4·5–6·2	4·5–6·0	4·0–5·0	—
Cellulose acetobutyrate	3·5–6·5	—	3·2–6·0	—
Cellulose nitrate	6·7–7·3	—	6·15	—
Ethyl cellulose	2·8	2·5–3·5	2·0–3·0	—
Polystyrene	2·6	2·6	2·6	2·9
Polythene	—	—	—	—
Polyvinyl chloride (plasticised)	4·0–12·0	4·0–12·0	—	—
Polyvinyl chloride-acetate (no filler)	3·2–3·5	—	3·0–3·3	4·0
Polyvinyl chloride-acetate (filled)	—	4·7	4·0	—
Polyvinyl formal	3·8	3·8	3·7	—
Polyvinyl butyral	3·7	3·7	3·5	—
Polyvinyl alcohol	—	—	—	—
Polyvinylidene chloride	3·0–·50	3·0–5·0	3·0–5·0	3·0–5·0
Methyl methacrylate (cast)	3·5	3·2	3·2	—
Methyl methacrylate (moulded)	3·0–3·1	3·3–3·5	3·1–3·3	—
Nylon	3·2	3·3	3·6	—
Casein	—	—	6·2–6·5	—

TABLE 182—POWER FACTORS FOR PLASTICS

Material	Power Factor			Radio Frequencies
	@ 50 cycles	@ 10^3 cycles	@ 10^6 cycles	
Phenol-formaldehyde (no filler)	·05–·10	·025–·06	·015–·04	·005–·05
Phenol-formaldehyde (wood flour filler)	·04–·30	·04–·15	·035–·10	·01–·1
Phenol-formaldehyde (mineral filler)	·10–·30	·10–·15	·005–·10	·1–·1
Phenol-formaldehyde (scrap fabric filler)	·08–·03	·08–·20	·04–·10	·05–·1
Phenol-formaldehyde (paper laminated)	—	—	·02–·05	·015–·05
Phenol-formaldehyde (fabric laminated)	—	—	·02–·08	·05–·1
Phenol-formaldehyde (asbestos laminated)	—	—	—	—
Phenol-formaldehyde (cast)	·025–·20	·005–·08	·01–·045	·005–·05
Phenol-formaldehyde (glass fabric laminated)	—	—	—	—
Phenol-furfural (wood flour filler)	—	·04–·15	·035–·10	·01–·06
Urea-formaldehyde (moulded)	·03–·15	·035–·065	·03–·04	—
Melamine (filled)	·07–·17	—	0·04	—
Cellulose acetate (sheet)	·02–·07	—	·04–·09	—
Cellulose acetate (moulded)	·01–·6	·02–·06	·04–·06	—
Cellulose acetobutyrate	·014–·06	—	·018–·05	—
Cellulose nitrate	·06–·15	—	·07–·10	—
Ethyl cellulose	—	·005–·025	·007–·03	—
Polystyrene	·0001	·0001	·0001	0·0002
Polythene	·0003	·0003	·0003	·0003
Polyvinyl chloride (plasticised)	0·136	—	—	—
Polyvinyl chloride-acetate (no filler)	·01–·04	·014	·018	0·018
Polyvinyl chloride-acetate (filled)	·04–·048	—	·01–·03	—
Polyvinyl formal	·007	·008	·009	—
Polyvinyl butyral	·06	—	—	—
Polyuinyl alcohol	—	—	—	—
Polyvinylidene chloride	·03–·08	·03–·05	·03–·05	—
Methyl methacrylate (cast)	·06	·06	·025	0·02
Methyl methacrylate (moulded)	·05–·06	·06–·07	·02–·03	0·02
Nylon	0·01	·015	·022	—
Casein	—	—	·050	—

The test piece is placed between two cylindrical brass electrodes, the faces being in contact with the test piece. The upper electrode is pressed down on to the test piece by means of a 5 lb. weight. Alternating current is applied at the desired frequency. The r.m.s. value of the voltage is measured by means of a suitable voltmeter. The voltage is raised from zero to breakdown as rapidly as can be measured.

Permittivity and Power Factor. Permittivity or dielectric constant is the ratio of the capacity of a condenser having the plastic as the dielectric compared with the same condenser having air as the dielectric. It will vary with the frequency of the alternating current which is used.

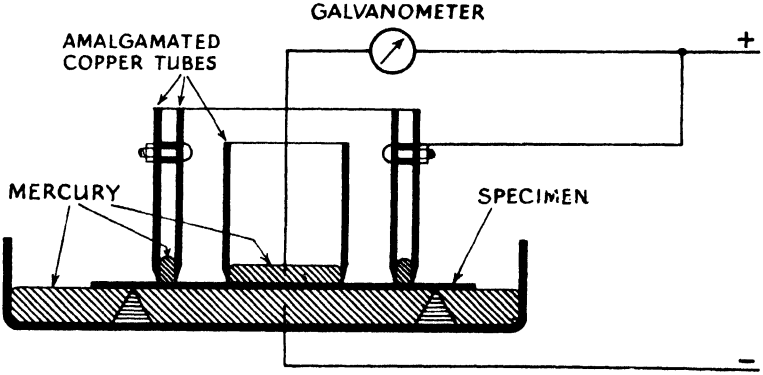


Fig. 265. Electrical connections for volume resistivity tests.

The power factor is the ratio of the power loss in the plastic when used as the dielectric compared with the total power transmitted through the condenser (product of the applied voltage and the resulting current). It varies with the frequency.

In the past, apart from the few materials intended for electrical insulation, these properties have not been of particular interest. Latterly they have gained new significance even where these properties are poor. The reason is the introduction of high-frequency heating methods. For these purposes low dielectric constant and high power factor are quite desirable features, in great contrast to normal electrical applications. In fact, those materials with particularly good electrical properties, e.g. polystyrene and polythene cannot be heat treated with high-frequency current.

From the point of view of communications the behaviour of the leading materials at extremely high frequencies, e.g. up to 3,000 megacycles, is of the highest importance.

To determine these values B.S.S. requires a flat sheet of material greater than 8 inches in diameter, between 3 and 6 m.m. thick. Electrodes and a guard ring are fitted to the test piece. These are made up of graphite and brass backing plates. The lower electrode is a 20 cm. circle. The upper electrode is also a circular of 15 cm. diameter, and is surrounded by a guard ring 15·4 cm. internal diameter. These areas are painted over with a graphite dispersion and then exactly covered by the brass plates. The measurements are determined by means of a Schering bridge, in which the test piece and electrodes form one capacitor. The most widely used test frequency is 800 cycles per second. The details of the test and methods of calculation are to be found in B.S.S. 903.

The characteristics of a number of other non-plastic materials which find application in the electrical field are quoted in the following Table. They may form the basis for comparison with the plastics. The one feature that should perhaps be emphasised is that apart from hard rubber (or ebonite) none of these materials can be machined. This contrasts with the excellent machining behaviour of most plastic materials.

Influence of Temperature on Plastics. By definition the behaviour of plastics towards temperature is one of their most critical properties. This behaviour imposes the principal limitations upon the use of plastics. From the practical point of view, other thermal considerations are no less important. In moulding operations the coefficient of expansion and subsequent shrinkage upon cooling will be a major factor. The amount of heat required and the nature of heating equipment will be influenced by the thermal conductivity of the material, and so on.

TABLE 183

PROPERTIES OF SOME NON-PLASTIC ELECTRICAL INSULATING MATERIALS

Material	Specific Gravity	Tensile Strength p.s.i.	Dielectric Constant	Power Factor		
				50 cycles	1 kc.	1 mc.
Mycalex . .	3·5	6,000– 8,000	6·8	—	·006	·003
Steatite . .	2·5	8,000–10,000	6·1	·01	·004	·003
Porcelain (dry process)	2·3	2,000– 3,000	6·2–7·5	·02	·01	·007
Mica . .	2·8	—	7·0–7·3	·0003	·002	·0002
Quartz (fused)	2·21	7,000–10,000	4·2	·003	·003	·0003
Glass . .	2·25	—	4·5	—	·005	·002
Hard Rubber	1·15	4,000– 7,000	2·3	·01	·01	·005–·009
Slate . .	2·8	5,000	6–8	—	·009	—

Thermosetting resins being infusible are not subject to marked flow with rise in temperature. On the other hand, thermoplastic materials will begin to flow as the temperature is raised. It is one of the defects of most thermoplastic materials that the flow temperature is lower than would be desired. With one or two exceptions this is general. In some instances it is possible to increase the softening point by the judicious addition of filling materials, etc. This practice almost invariably introduces other disadvantages.

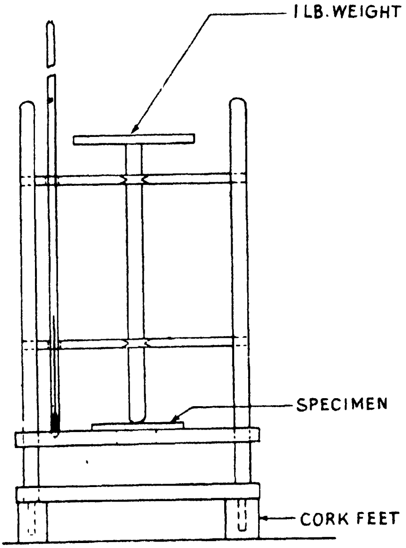


Fig. 266. Arrangement for softening point test for thermoplastics

Softening Point. The most important characteristic is the softening point or the temperature at which thermal deformation begins. Above this temperature the material becomes progressively faster and flows more readily until a condition approximating to a melting point is reached, when the material behaves substantially as a fluid. There is no definite softening point. As the temperature rises the material changes from a more or less rigid condition with barely any flow to a softer comparatively fluid state. With most plastics this softening range is very wide. It is a characteristic of typically amorphous materials. The exceptions are the materials which show crystallised behaviour, namely, nylon, polythene and polyvinylidene chloride. Each of these has a fairly sharp melting point and a very narrow softening range.

There are a number of different methods employed to determine the softening point. One method is based on the familiar ball and ring test, such as is widely used for bituminous materials and waxes, etc.

The Ball-and-Ring Method for Softening Point. The equipment consists of a brass ring ⅝ inch inside diameter, 3/32 inch thick, and ¼ inch deep. This is supported so that the lower surface is exactly an inch above a flat brass plate. The plastic is either melted and poured into this ring, or may be moulded into the ring. The assembly is placed into a glass vessel containing distilled water. A steel ball ⅜ inch in diameter, weighing 3·5 grams, is placed in the middle of the material in the ring. The temperature of the water is then raised at a rate of

TABLE 184

MAXIMUM OPERATION (CONTINUOUS) TEMPERATURES FOR PLASTICS

Material	Maximum Operation Temp. (° C.)
Phenol-formaldehyde (no filler)	120
Phenol-formaldehyde (wood flour filler)	175
Phenol-formaldehyde (mineral filler)	230
Phenol-formaldehyde (scrap fabric filler)	120–175
Phenol-formaldehyde (paper laminated)	100–150
Phenol-formaldehyde (fabric laminated)	100–175
Phenol-formaldehyde (asbestos laminated)	200–230
Phenol-formaldehyde (cast)	72
Phenol-formaldehyde (glass fabric laminated)	250
Phenol-furfural (wood flour filler)	230
Urea-formaldehyde (moulded)	72
Melamine (filled)	150–200
Cellulose acetate (sheet)	60–80
Cellulose acetate (moulded)	60–80
Cellulose acetobutyrate	60–90
Cellulose nitrate	60
Ethyl cellulose	60–80
Polystyrene	65–75
Polythene	80
Polyvinyl chloride (plasticised)	65
Polyvinyl chloride-acetate (no filler)	110
Polyvinyl chloride-acetate (filled)	—
Polyvinyl formal	70–100
Polyvinyl butyral	60
Polyvinyl alcohol	100
Polyvinylidene chloride	130
Methyl methacrylate (cast)	60–70
Methyl methacrylate (moulded)	60–70
Nylon	—
Casein	60

5° C. per minute. The temperature recorded when the steel ball touches the top of the lower plate is taken as the softening point. For softening points above 80° C. glycerine is used instead of water.

Halls[7] has described a simple method which is related to the Ball-and-Ring procedure. The softening point determinations on the thermoplastics were made on a plunger type of test, using the apparatus shown in Fig. 266. It comprises a framework carrying two horizontal plates,

½ inch apart, the upper one 0·20 inch thick, having a central hole of ½ inch diameter. The specimen, reduced by machining to $\frac{1}{16}$-inch thickness, is laid over this hole and the plunger brought to rest upon it. The plunger is ¼-inch diameter, and operates freely between two guides. The platform at its upper end is loaded to a weight of 1 lb. inclusive of the plunger itself. The whole set-up can be heated gradually by means of a water bath at a rate of 5° C. per minute. The softening point of the specimen is read as that at which the extruded sheath of plastic reaches the lower plate, or at which the extruded dome fractures, whichever first occurs. This temperature is indicated by a thermometer in the bath, which, of course, must be kept stirred to maintain uniformity of heat throughout.

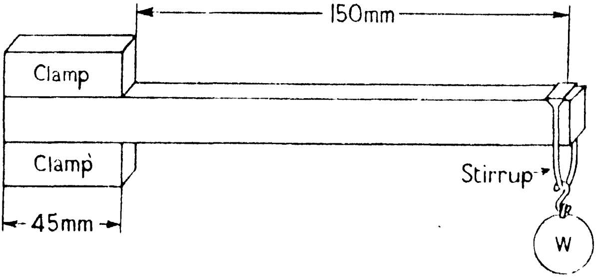


Fig. 267. Test for plastic yield

Another is the determination of the plastic yield of a cantilever test piece under a fixed load as the temperature is increased. Plastic yield is the total deformation of a bar-shaped specimen stressed under cantilever loading at a given temperature for a given time. This test features in most specifications. In British Standard Specifications 771 and 903 it is described as a proof test.

A bar 200 mm. long and 15 mm. square section, with a V-notch across one side 5 mm. from the end is mounted horizontally as a cantilever. It is rigidly clamped at one end (see Fig. 267) so that A = 45 mm. and B = 150 mm. The stirrup is such as to distribute the load uniformly across the width of the test piece. The test piece is heated for 15 minutes at the test temperature (see below), the height of the stirrup above a fixed point measured, and a load of 450 g., including the weight of the stirrup, is applied by means of the stirrup. The test piece is kept under load at the test temperature for six hours, at the end of which period, with the load still in position, the height of the stirrup shall be remeasured. It must not have dropped more than 5 millimetres. The method is adapted to find the actual yield temperature, i.e. when the yield does amount to 5 millimetres. This is done by repeating the tests at increasing temperature intervals until the yield is reached.

In the case of the Martens test, the load is much higher, being equivalent to 50 kg. per sq. cm. The set-up is similar, but the temperature is raised 50°C. per hour until the deflection reaches 6 mm. The Martens test is much more rapid than the British test, but is said to give higher results.

TABLE 185

THERMAL EXPANSION OF PLASTICS

Material	Thermal Expansion (in./inch/°C.)
Phenol-formaldehyde (no filler)	—
Phenol-formaldehyde (wood flour filler)	·000037–·000075
Phenol-formaldehyde (mineral filler)	·000025–·000040
Phenol-formaldehyde (scrap fabric filler)	·000020–·000060
Phenol-formaldehyde (paper laminated)	·000017–·000025
Phenol-formaldehyde (fabric laminated)	·000017–·000030
Phenol-formaldehyde (asbestos laminated)	·000017–·000025
Phenol-formaldehyde (cast)	·000028
Phenol-formaldehyde (glass fabric laminated)	—
Phenol-furfural (wood flour filler)	·000030
Urea-formaldehyde (moulded)	·000025–·000030
Melamine (filled	—
Cellulose acetate (sheet)	·000140–·000160
Cellulose acetate (moulded)	·000140–·000160
Cellulose acetobutyrate	·000130–·000150
Cellulose nitrate	·000120–·000160
Ethyl cellulose	·000100–·000140
Polystyrene	·000070–·000080
Polythene	·0001
Polyvinyl chloride (plasticised)	—
Polyvinyl chloride-acetate (no filler)	·000069
Polyvinyl chloride-acetate (filled)	—
Polyvinyl formal	—
Polyvinyl butyral	·00015
Polyvinyl alcohol	—
Polyvinylidene chloride	·00019
Methyl methacrylate (cast)	·000080
Methyl methacrylate (moulded)	·000080–·000090
Nylon	·0001
Casein	·000080

Shrinkage. The shrinkage of plastics particularly during the moulding cycle is obtained by direct measurement. The B.S.S. test moulds a specimen 4 to 5 inches in diameter and 0·125 inches thick, under prescribed conditions. After cooling, the dimensions are measured and the difference between these values and the original values gives a measure of the shrinkage.

There will be other forms of shrinkage. Where plastics contain plasticisers, etc., which are volatile there will, in due course, be some losses and corresponding shrinkage. When plastics are subjected to continuous raised temperature, there may be continued polymerisation or internal chemical effects which may be shown by shrinkage. This angle has been studied by Goggin.[6]

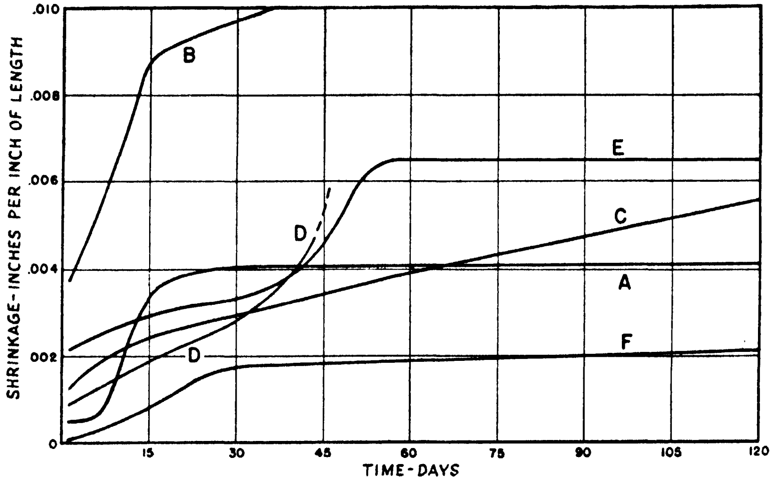


Fig. 268. Dimensional stability of plastics at 50°C.[6]

A. Phenol-formaldehyde. B. Cellulose acetate. C. Cellulose acetobutyrate. D. Methyl methacrylate. E. Ethyl cellulose. F. Polystyrene

Cold Flow. In its narrowest sense "cold flow" is considered to be the degree of deformation which a material will experience under its own weight. It becomes increasingly more apparent as the temperature rises. Where it is at all marked then such materials are very restricted in use. However, under applied loads most materials tend to undergo a certain amount of flow over a period of time. Another way to express this is the creep under load. The extent to which this occurs is clearly a matter of great significance where dimensional uniformity and stability must be maintained. In some instances the property can be an advantage as in packings, seals, etc. But in most applications it is a disadvantage. As might be expected cold flow is most marked in thermoplastic materials.

Bunn and Hopkins[2] have made a study of the relative cold flow of a number of plastic materials. The results are summarised in the following Table.

TABLE 186

MEASURED PERCENTAGE DECREASED IN HEIGHT OF ½-INCH CUBE HELD FOR 24 HOURS AT 100° C. BETWEEN PARALLEL PLATES UNDER LOAD OF 1000 LB.

Material	Cold Flow %
Phenolic plastics	0·4
Urea plastics	0·7 to 7
Cast phenolics	10·0
Hard rubber	0·5 up to 80
Vinyl plastics	1·0 up to 32
Acrylic resins	1·0 up to 50
Polystyrene	1·0 up to 22
Cellulose acetate plastics	2·0 up to 64
Benzyl cellulose	76·0

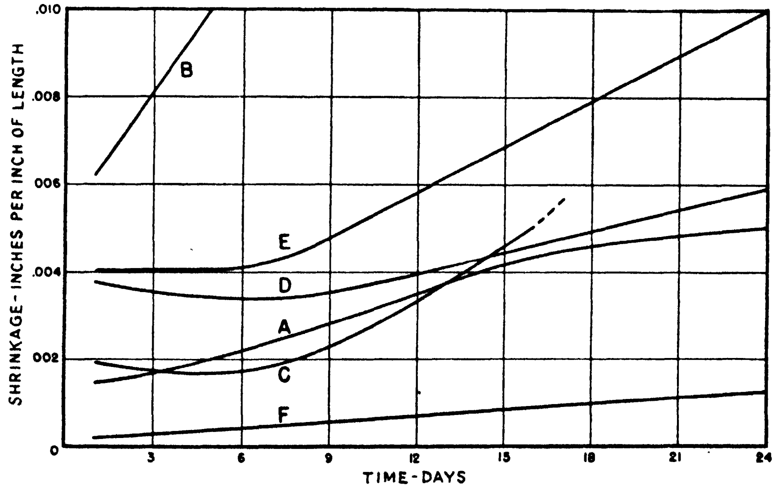


Fig. 269. Dimensional stability of plastics at 70° C.[6]

The Hardness of Plastics. The hardness of plastics is a matter of some importance for many applications. In many respects it gives some indication of such factors as scratch resistance, obviously a primary consideration for transparent materials, etc.

So far as testing is concerned, the materials must be considered in two categories, the soft yielding rubber-like plastics and the hard rigid materials. Different methods are employed to assess the hardness in each instance. The general principle is to consider indentation caused by a known load.

The Brinell method of hardness is carried out by pressing a steel ball into the surface under test. Usually in metal practice a ball with a 1 c.m. diameter is pressed under a force of between 500–3000 kilograms. In the case of relatively soft materials such as plastics, a much smaller ball and smaller load is applied. Thus common practice is to employ a 2·5 mm. ball with a load of 25 kilograms.

TABLE 187

BRINELL HARDNESS OF PLASTICS

Material	2·5 mm. Ball 25 kg. Load
Phenol-formaldehyde (no filler)	30–45
Phenol-formaldehyde (wood flour filler)	—
Phenol-formaldehyde (mineral filler)	—
Phenol-formaldehyde (scrap fabric filler)	32–40
Phenol-formaldehyde (paper laminated)	24–40
Phenol-formaldehyde (fabric laminated)	30–45
Phenol-formaldehyde (asbestos laminated)	30–45
Phenol-formaldehyde (cast)	30–45
Phenol-formaldehyde (glass fabric laminated)	—
Phenol-furfural (wood flour filler)	35–40 (50 Kg.)
Urea-formaldehyde (moulded)	48–54 (500 Kg., 1 cm. ball)
Melamine (filled)	—
Cellulose acetate (sheet)	8–15 (10 Kg.)
Cellulose acetate (moulded)	
Cellulose acetobutyrate	
Cellulose nitrate	
Ethyl cellulose	
Polystyrene	20–30
Polythene	—
Polyvinyl chloride (plasticised)	—
Polyvinyl chloride-acetate (no filler)	15–25
Polyvinyl chloride-acetate (filled)	—
Polyvinyl formal	—
Polyvinyl butyral	—
Polyvinyl alcohol	—
Polyvinylidene chloride	—
Methyl methacrylate (cast)	18–20
Methyl methacrylate (moulded)	14–21
Nylon	—
Casein	23

As might be expected, methods adopted for the softer rubbery materials follow rubber practice. The Shore durometer is widely employed. In Great Britain the hardness equipment designed by the R.A.B.R.M. has been generally adopted and is recommended in B.S.S. 903. For example, the test recommended for polyvinyl chloride compounds among British cable-makers is as follows:

Hardness Number. Test pieces are 10 mm. thick and of sufficient area for the tests to be taken at not less than 12 mm. from the edge. The upper and lower surfaces are as flat and smooth as possible.

The polyvinyl chloride compound test piece is supported on a horizontal, rigid surface. Temperature is maintained at 20°C. A plunger terminating in a rigid ball 3/32 inch (2.38 mm.) diameter is pressed for five seconds vertically on to the test piece, the load on the ball being 30 g., and the position of the plunger noted. An additional load of 535 g. is then applied and maintained for 30 seconds, and the position of the plunger is then read again. The part of the plunger in contact with the test piece shall nowhere exceed 3/32 inch diameter. During the loading periods the apparatus is gently vibrated, preferably by means of a buzzer, to overcome any friction. The movement of the plunger, i.e. the difference between the two readings, expressed in 100ths of a mm., is the Hardness Number.

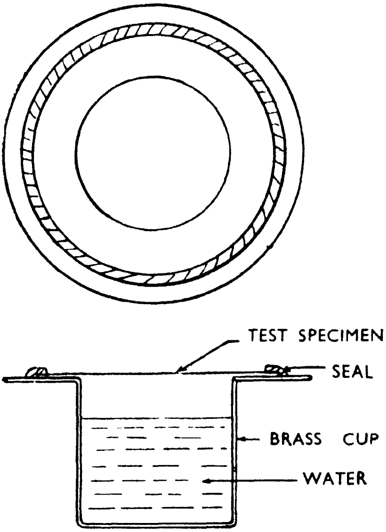


Fig. 270. Set-up for water vapour permeability test

Water Permeability of Plastics. In the case of films of material it is particularly important that they should be impermeable to water. In many cases such films are used as a protection against moisture, for moisture-proofing. The first inclination is to think that this behaviour will follow closely the water absorption properly. Actually this is not the case. An entirely different set of conditions applies. The structure of the material plays a great part. The outstanding example is the case of polystyrene, whose water absorption over indefinite periods is nil. Yet a film of polystyrene is relatively permeable to water. The best known material as regards water permeability is polyvinylidene chloride.

This neither absorbs water, nor does it allow it to pass through even the thinnest of films.

Comparative tests have been made on films of various plastics. The results are shown in the Table.

Tests were made by sealing the specimen over a brass cup containing water, using a moisture-proof sealing compound. This set-up is shown diagrammatically in Fig. 270. The assemblage was weighed initially and at intervals during exposure to a dry atmosphere in a desiccator containing calcium chloride as drying agent. The approximate area of specimen exposed and through which water vapour could pass was 1 sq. inch. The specimen was, therefore, submitted to conditions of 100 per cent humidity gradient, that is, 100 per cent humidity within the cup, 0 per cent in the outside atmosphere, at laboratory temperature. The results given in the Table are expressed in terms of milligrams of moisture vapour passing through an area of 1 sq. inch of the film under these conditions.

TABLE 188

WATER PERMEABILITY OF FILMS

Material	Film Thickness (″)	Water Milligrams/sq. in./day	
Cellulose acetate (sheet)	0·002	168	(1,040)
Cellulose acetatebutyrate	—	—	—
Cellulose nitrate	—	—	—
Ethyl cellulose	0·001	1,000	—
Polystyrene	0·0025	0·7	(5)
Polythene	—	—	—
Polyvinyl chloride (plasticised)	—	—	—
Polyvinyl chloride-acetate (no filler)	—	—	—
Polyvinyl chloride-acetate (filled)	—	—	—
Polyvinyl formal	—	—	—
Polyvinyl butyral	0·010	5–8	—
Polyvinyl alcohol	—	—	—
Polyvinylidene chloride	0·0014	nil	(nil)
Nylon	—	—	—
Regenerated cellulose	0·001	750	(7,300)
Moisture-proof regenerated cellulose	0·001	20	(145)
Rubber hydrochloride	0·001	5	(33)

The measurement of viscosity is a matter of great importance in many plastics activities. The viscosity of solutions is accepted as giving a measure of the chain length or degree or polymerisation of many polymers.

Apart from this the flow characteristics of the actual solutions are extremely important since so many plastics operations are conducted with such solutions. Examples include the casting of films, the coating of fabrics, the spreading of adhesives and so on. A number of methods are employed, some very accurate and able to give absolute viscosities, others design to give relative viscosities. Some methods are designed for rapid control-testing under works conditions.

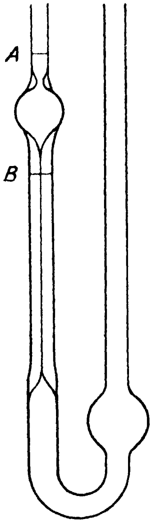


Fig. 271. Ostwald viscometer

Ostwald Viscometer. The leading method for determining viscosity is based on the Ostwald Viscometer. This is shown in the figure and consists of two bulbs connected by a capillary tube. Marks are etched above and below the first bulb. The other bulb is filled with the material to be tested. This is drawn into the other part of the apparatus until the liquid surface is above the upper mark. The time required for the solution level to fall to the lower mark is noted. The times taken for different liquids give a measure of the relative viscosities. Absolute viscosity in centipoises is found from this by taking the time required for a liquid of known viscosity. When this is known the viscosity is given by $\frac{n}{n_0} = \frac{td}{t_0 d_0}$ where n is the desired viscosity, n_0 = viscosity of standard, t and t_0 respective times of flow and d and d_0 the respective densities.

Experiments must be carried out at constant temperature since temperature has a profound effect on the viscosity.

Falling Ball Method. Methods for determining viscosity have been established by the British Standards Institution. In B.S.S. 188/1937 they describe the Ostwald type of viscometer and the Falling Ball method and lay down prescribed conditions. Viscosity measurements must always be made under conditions of constant temperature for viscosity is very critical to temperature change.

The Falling Ball method is extremely convenient, involving simple equipment. Steel balls of specified dimensions are allowed to fall through the solution under test, and the time taken between two marks is measured. They are readily available as standard steel balls used for ball bearings. Obviously the method only applies to clear solutions.

TABLE 189

Range of Viscosity in Centistokes.	Diameter of Ball.	
	mm.	in.
1,000 to 5,000	1·50	1/16
5,000 to 12,000	2·38	3/32
12,500 to 25,000	3·18	1/8

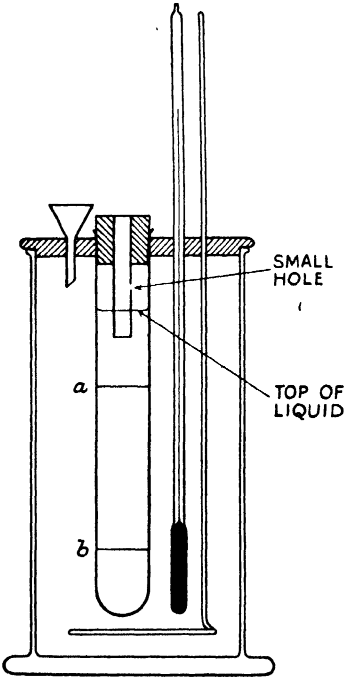


Fig. 272. Standard falling sphere viscometer

The tube must be at least ten times the diameter of the ball to be used.

A tube 32 mm. in diameter is suitable for the sizes of sphere specified above. The standard distance over which the fall of the sphere is timed is 150 mm., two reference marks this distance apart being provided on the tube as shown (*a*, *b*). The length of the tube is such that the reference marks are approximately equidistant from the two ends of the tube, this distance from the ends being not less than 55 m.m. in either case. The liquid is allowed to stand until it is free from bubbles.

The time taken for the ball to fall between the two marks is measured by an accurate stop watch, several readings are taken.

Gibson[5] and Jacobs recommend the use of pure glycerine S.G. 1·2589 at 20° C. as a standard for the falling ball method, having a viscosity of 10·24 in absolute units.

Hercules Falling Sphere Method. The Hercules falling sphere method used in America uses the following solution:

	Per cent.
Dry nitro-cellulose	12·2
Denatured alcohol	22
Ethyl acetate	17·5
90° Benzole	48·3

The solution is placed in a 1 inch glass tube, and the time taken for a $\frac{5}{16}$ in. steel ball (weight 2·046–2·054 grams) to fall through 10 inches of the solution is taken as the viscosity of the grade in question, whether $\frac{1}{2}$ second, 4 seconds, etc. There is a mark 2 inches from top and 2 inches from the bottom. One disadvantage of this method is that a very small time has to be measured in the case of low viscosity cottons, and this is surmounted by using more concentrated solutions of these types.

Another objection is that the solvents used are liable to vary, not being pure materials.

In the case of cellulose acetate a convenient solution is found to be 20 per cent in 9 parts of acetone and 1 of alcohol.

A rather better method seems to be that of Messrs. Nobel Industries, Ltd., which employs a purer solvent and a $\frac{1}{16}$ inch falling sphere to give easier timing. According to the grade of nitro-cotton, 10, 20 or 40 grams of dry sample are dissolved in 100 c.c. of commercially pure acetone diluted to S.G. 0·810 at 15·5°C. with distilled water. At a temperature of 20°C. if the time of fall is T seconds then absolute viscosity is approximately $\frac{T}{2}$.

Ostwald Resin Viscosities. A 16-mm. diameter steel ball is allowed to fall through a distance of 250 mm. in a solution of the resin diluted with an equal amount of acetone contained in a 30-mm. tube. The value is given as a ratio being:

$$\frac{\text{Time of fall in } 1/100 \text{ seconds of resin solution}}{\text{Time of fall in } 1/100 \text{ seconds in pure acetone}}$$

Thus, if it is 20/100th minutes for acetone and 160/100th minutes for resin solution, the figure is Ostwald 8.

The Redwood Viscometer. The most popular routine standard viscosity method employs the Redwood Viscometer.

The normal viscometer consists of a copper silver cylinder which contains the liquid to be tested. Enough material is used so that an indicator is just covered. The base of the cylinder contains an agate orifice which is closed by a valve attached to a rod. The whole viscometer is jacketed in order to maintain any desired temperature. Beneath the outlet is a narrow-necked flask graduated with a mark representing 50 c.c. To determine the viscosity the valve is opened and the time required for 50 c.c. of material to flow through the orifice into the flask is recorded. It is expressed by the number of seconds taken.

A simple and rapid method for finding the relative viscosity of a solution is to compare the times taken for 25 c.c. to run out of a pipette.

K-Value to indicate Molecular Weight. The Germans have classified their plastic materials by means of the "K-values" which indicate the degree of polymerksation of plastic materials. This work is based upon the fundamental studies of Fikentscher and Mark,[4] and of Fikentscher.[3] The latter author gives the equation:

$$\frac{\log (N_s/N)_0}{c} = \frac{75\ K^2}{1+1\cdot 5\ Kc} + K$$

where N_s = viscosity of solution, concentration below 5% polymer.
N_0 = viscosity of solvent in the same viscometer.
c = concentration of polymer in grams/cc. of solution.
K = a parameter characteristic of the polymer.

The K-value is determined by solving this equation with data upon one solution of a polymer, expressing concentration in grams/100 cc. of solution and multiplying the K- found by 1,000. This is used in characterising polyvinyl chloride, polyvinyl acetate, polystyrene, etc. For the cellulose derivatives, the general practice was to multiply the K- found in the equation by 10,000.

For polyvinyl chloride, K-values were calculated from viscosity measurements on a solution of 1 gram of the polymer in 100 cc. of cyclohexanone, measured in a Hoeppler viscometer in centipoises at 25°C. For polystyrene, benzene was used as the solvent; this also was used for polyvinyl acetate. For these products, K-values of 40 to 100 were generally found. The cellulose derivatives were generally measured in dilute acetone solutions, K-values ranging from 450 to 1,440 being given for nitro-cellulose, while the cellulose acetate ranged from 7,000 to 10,000 in K-value. In his original article Fikentscher states that for cellulose acetate, polystyrene, etc., the K-value will not vary more than ± 10 per cent if different solvents are used, while the K-values for nitro-cellulose may vary as much as 20 per cent with different solvents, over a range of concentrations from 1 per cent to 15 per cent polymer.

The advantages of the K-value in characterising the molecular size of polymers are:

(1) With a single viscosity measurement, the course of the viscosity-concentration curve is located, within the limits of error given, for solution concentrations between 1 and 15 per cent.

(2) Only a simple arithmetic process is necessary to estimate the average K-value of a blend of two polymers. If P_1 is the percentage of component of K-value K_1 and P_2 is the percentage of component of K-value K_2, the K-value Kb of the blend may be calculated from the relation:

$$Kb=(P_1K_1+P_2K_2)/(P_1P_2)$$

where $P_1+P_2=100$

Molecular-weight-distribution. In the polyvinyl chlorides, two tests, the M-number and the Defo value, were used to roughly characterise the heterogeneity of the polymers manufactured.

The M-number gives some indication of the number of short chains present in the polymer. The M-number was defined as the number of grams of solvent (a mixture of 1 part monochlorbenzene and 3 parts epichlorhydrin) that will dissolve 1 gram of Igelit PCU at 80°C. and then gel within 3 minutes when cooled to 20°C. Strictly a cut and try method, it will vary somewhat with different operators.

Defo Value. The Defo number of various materials was a very important figure in everyday German production. The Defo value is supposed to measure the number of long chains present. The test sample is made by milling 60 parts of Igelit PCU with 40 parts of tricresyl phosphate at 160°C. for 20 min. The plastic is then compressed while hot into a cylinder 10 mm. in diameter and 10 mm. high. It is cooled, its height measured and it is placed in an oven at 100°C. (70°C. for Igelit MP series), loaded with a two-kilogram weight, and heated under load for 24 hours. It is then removed from the oven, cooled to room temperature, and the height again measured. The Defo value is the percentage of the original height which is lost.

A somewhat different Defo test was used for synthetic rubber. This has been defined as the force in grams required to compress a Buna cylinder 10 mm. high and 10 mm. in diameter to a height of 4 mm. in 30 sec., at 80°C. After a release period of 30 sec., the height of recovery in hundredths of a millimeter is measured, and expressed as a percentage of the original height. This two digit number is frequently, but not always, found with the Defo number. Buna S delivered to the manufacturing plants had a Defo of over 3,000, apparently corresponding to a Mooney of 160. It was softened in warm air, and for tyres was used at a Defo of around 700, which probably corresponds to a Mooney of about 55.

REFERENCES

1 British Standards Specifications for Plastics:
- B.S. 316, Synthetic-Resin Varnish-Paper Boards and Tubes for Electrical Purposes.
- B.S. 474, Synthetic Resins (Phenol-Aldehyde Type) for the Manufacture of Boards, Tubes and Cylinders.
- B.S. 488, Moulded Insulating Materials suitable for Accessories for General Electric Installation.
- B.S. 547, Synthetic-Resin Bonded-Paper Sheets (Grade 1) for Electrical Purposes.

B.S. 668, Laminated Synthetic Resin Bonded Sheet (Fabric Base) for use as Gear Material.
B.S. 771 (Synthetic-Resin (Phenolic) Moulding Materials and Mouldings.
B.S. 972, Synthetic-Resin Bonded Fabric Sheet for Electrical and Mechanical Purposes.
2 Burns and Hopkins. *Mod. Plast.*, 1937, August, p. 42.
3 Fikentscher. *Cellulose chemie*, 1932, **13**, 58.
4 Fikentscher and Mark. *Kolloid-Z.*, 1929, **49**, 135.
5 Gibson and Jacobs. *J.C.S.*, 1920, **117**, 473.
6 Goggin. *Chemical Industries*, December 1939.
7 Halls, *Plastics,* 1943, **7**, 74.
8 Livingston Smith. *British Plastics*, 1943, **15**, 391.
9 Piech and Gloor. *A.S.T.M. Bulletin*, 1948, **151**, 70.

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