

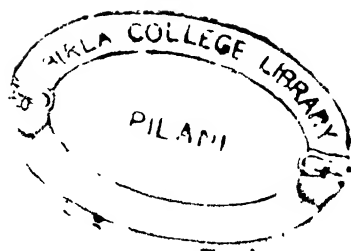
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SYNTHETIC RESINS AND ALLIED PLASTICS

BY VARIOUS AUTHORS

Edited by

R. S. MORRELL, M.A., Sc.D., Ph.D., F.I.C.
HON. RESEARCH TUTOR, WOLVERHAMPTON AND
STAFFORDSHIRE TECHNICAL COLLEGE

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LIST OF CONTRIBUTORS

- J. R. ALEXANDER, M.A., B.Sc., Ph.D. (*Messrs. Wm. Walker & Sons, Ltd., Bolton*).
- E. A. BEVAN, B.Sc. (*Technical Manager, Messrs. Beck, Koller and Co. (England), Speke, Liverpool*).
- R. P. L. BRITTON (*Messrs. Hadfields (Merton), Ltd., Mitcham*).
- E. G. COUZENS, B.Sc., A.R.C.S. (*Assistant Factory Manager, B.X. Plastics, Ltd., Manningtree*).
- ROWLAND HILL, Ph.D., B.Sc. (*I.C.I. (Dyestuffs), Blackley, Manchester*).
- H. M. LANGTON, M.A., B.Sc. (*Consulting Chemist*).
- H. S. LILLEY, B.Sc. (*I.C.I. (Paints), Ltd., Slough*).
- R. S. MORRELL, M.A., Sc.D., Ph.D., F.I.C. (*Hon. Research Tutor, Wolverhampton and Staffordshire Technical College*).
- C. A. REDFARN, Ph.D., B.Sc., F.I.C. (*Consulting Chemist*).
- V. E. YARSLEY, D.Sc., M.Sc., F.I.C. (*Consulting Chemist*).

PREFACE TO THE SECOND EDITION

SINCE the first edition appeared in 1937 the progress in the development and uses of synthetic resins and plastics has increased by leaps and bounds. The range of the subject has become so wide that discussion of it by only four collaborators became quite inadequate, and experts were invited to co-operate to give authoritative representation of the chief sections of the synthetic resins and allied plastics. The protein and cellulosic plastics have been dealt with by Dr. V. E. Yarsley; the phenol-formaldehyde and urea-formaldehyde resins and their plastics have been described by Dr. C. A. Redfarn; Dr. Rowland Hill of the I.C.I. (Dyestuffs), Blackley, Manchester, has summarized the knowledge of the vinyl and acrylic acid resins; Mr. H. S. Lilley of the I.C.I. (Paints), Slough, the phenolic resins in varnish and enamel manufacture; and Dr. J. R. Alexander, Messrs. Wm. Walker & Sons, Bolton, the urea-formaldehyde and melamine resins for varnish compositions. Mr. E. A. Bevan of Messrs. Beck, Koller and Co. (England) has written on the alkyd resins and their recent developments, and Mr. E. G. Couzens (B.X. Plastics, Ltd., Brantham Works, Manningtree) has described the methods of identification and testing of resins and plastics, a section which was dealt with very inadequately in the first edition. Mr. T. Hedley Barry, owing to special war work, has been unable to contribute, but Mr. R. P. L. Britton of Messrs. Hadfields (Merton), Ltd., Mitcham, is again responsible for a condensed account of the resins and plastics as electrical insulation materials. Mr. H. M. Langton has revised and brought up to date the General Introduction as well as the chapters on ester gums and coumarone and indene resins. Many chapters have been entirely rewritten, and it is hoped that errors and omissions in the previous edition have been remedied.

Wherever possible communications from less accessible journals, especially patent specifications, have been cross-referenced to British Chemical Abstracts, A and B, so as to assist the reader. The authors gratefully acknowledge their thanks to their respective firms for permission to collaborate in the compilation of this book; they also wish to acknowledge their appreciation of the kindness of the following firms and journals in allowing the reproduction of illustrations and diagrams:—Dr. H. I. Price of Messrs. N. H. Graesser, The Chemical Works, Sandycroft, Chester, for valuable comments on the section dealing with the production of phenols; Mr. J. L. Daniels of Messrs. T. H. & J. Daniels, for looking over the sections dealing with moulds and presses; Dr. W. Blakey of Messrs. British Industrial Plastics for reading the section on urea resins. And the following firms for the use of illustrations: Messrs. British Industrial Plastics; Bakelite, Ltd.; John Shaw & Sons (Salford), Ltd.; T. H. & J. Daniels, Ltd.; Messrs. Cellomold, Ltd.; and the British Standards Institu-

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tion. The Editor is grateful to Messrs. Mander Brothers, Ltd., for permission to undertake the revision of the first edition, to the Governors of the Wolverhampton and Staffordshire Technical College for facilities, and to Mr. L. L. Ruderman for his kindness in reading the proofs of the chapter on resins as electrical insulators.

R. S. M.

WOLVERHAMPTON AND STAFFORDSHIRE
TECHNICAL COLLEGE
January 1943

PREFACE TO THE FIRST EDITION

IN 1928, Hedley Barry, A. A. Drummond, and R. S. Morrell were the authors of *Natural and Synthetic Resins* (E. Benn, Ltd.). In 1932 Hedley Barry wrote *Natural Resins* (E. Benn, Ltd.) to bring the first section of the subject up to date. The present volume gives the advances made in the second section from 1928. Since that year there has been a vast amount of technical development with rapidly increasing varieties of application. In many cases the chemistry of synthetic resins is imperfectly understood and the theories as to the causes of resin formation are as yet often speculative, but co-ordination of physical and chemical properties is progressing.

The term 'synthetic' may be open to criticism in contrast to 'artificial', which is correct, except for its suggestion of inferiority. The *Oxford English Dictionary* defines synthesis as: 'combination, composition, putting together, artificial production of compounds from their components.' This definition legitimizes the title, although it is not the strict meaning of the term from a chemical standpoint, because none of the synthetic resins have the same chemical composition as the natural resins, yet they frequently contain the same chemical elements.

In the introductory chapter the object has been to give a summary of the chemical and physical properties of the most important classes, so that the reader interested in only one special group may obtain a general survey of the subject. The chapters on Plastics are essentially technical and the aim of the authors has been to collate the methods of preparation and the properties of the varieties. It is hoped that no important method of technique has been overlooked or inaccurately described. Resins of the varnish class cannot always be separated from those of the plastics variety and overlapping is unavoidable, especially in the chapter on Miscellaneous Resins. Under Electric Insulators an attempt has been made to correlate properties and chemical composition, an aspect which is not yet recognized by electricians. Under the Causes of Resinification the authors have tried to give the important facts and views of workers in that field. In the last chapter the lack of system in the analytical

methods is stressed strongly. A treatise on synthetic resins and allied plastics must be of the character of a compilation. Each class of industrial resins or plastics has its experts, who are seldom allowed to collaborate as authors. The present authors have confined themselves to a critical summary of the published literature on the subject. Such treatment may fail to satisfy specialists who look for expert knowledge in every section.

The authors wish to express their gratitude to Drs. J. O. Cutter, F. W. Skirrow, and E. E. Walker, and Mr. W. E. Wornum for reading sections of the manuscript and offering many valuable suggestions. They are much indebted to the kindness shown by the late Mr. W. Rossiter who read the section dealing with the Urea Resins and gave most valuable advice. They gratefully acknowledge the permission granted to use illustrations and diagrams supplied by the following firms and publishers: Baker, Perkins, Limited; John Shaw & Sons (Salford), Limited; Erinoid, Limited; The Beetle Products Company, Limited; the Plastics Press, Limited; and The Industrial Chemist. Two of the authors (R. S. M. and R. P. L. B.) acknowledge with thanks permission from Messrs. Mander Brothers, Limited, Wolverhampton, and Messrs. Hadfields (Merton), Limited, Mitcham, respectively, to assist in the compilation of this book.

R. P. L. B.
T. H. B.
H. M. L.
R. S. M.

September
1937

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All temperatures are given in degrees centigrade.

1 Ångström Unit = 10^{-8} cm.

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CHAPTER I
GENERAL INTRODUCTION

By H. M. LANGTON

NUMEROUS historical relics coupled with many references in ancient writings justify the inference that even in the pre-Christian era man was familiar with the use of resinous substances for decorative coatings. As the decorative arts developed in the Middle Ages, the use of resins increased, as mention in contemporary European literature bears witness. In modern times damars, copals, and other hard natural resins have been added to the list of those already in use.

The art of lacquering, based on the use of indigenous natural resins, originated in China and reached its highest development in Japan, where records of its use there go back to the fourth century. In India and the East shellac has long been used in the fashioning of moulded ornaments and in the manufacture of varnishes, and is to-day the principal spirit varnish resin in use throughout the world. But in the present century shellac has become more and more important as a moulding material by reason of its thermal plasticity, and its use in the manufacture of gramophone records accounts probably for 20,000 tons annually, the requirements of the electrical and varnish trades being next in order of importance.

Formerly, when speaking of resins, the term was accepted as referring solely to those natural secretions, mainly derived from coniferous trees, insoluble in water in which they would not gelatinize. Further, these secretions softened on heating and their solutions in alcohol and other organic solvents formed more or less adhesive liquids. Evaporation of these solutions gave films very resistant, on exposure, to the action of the weather and most chemical reagents. The cheapest and most commonly used varnish resin, though by no means the best, is colophony or rosin, the oleo-resin of many species of pine-tree. The increasing use of this material and of the other resins already mentioned in the varnish and allied plastic industries has stimulated the study of their chemical constitution and their physical properties. From such studies new lines of manufacture developed, and research followed the customary channels, endeavouring first to find substitutes, and next to synthesize new products simulating in properties and range of applicability the natural products it was hoped to supplement, if not indeed to supplant. During the present century, more especially during the past twenty years, the rise of the synthetic resin industry has been followed in its wake by the production of new plastic materials allied to the synthetic resins in some of their properties and in range of usefulness. For some requirements, synthetic resins are in special cases more suitable than natural resins in the varnish industries. By reason of their plasticity, many synthetic resins have proved so adaptable in the

moulding industry that whole fields of new manufacture have arisen, undreamt of a quarter of a century ago. To-day these related materials are of growing importance in the varnish industry, as protective and insulating coatings in the electrical industries, and most of all in the moulding trades. In laminated form, synthetic resins are now finding increasing use as constructional materials in interior furnishing in the building industries, in aircraft construction, mechanical engineering, and in the construction and lining of chemical plant. While some synthetic resins have properties akin to those of natural resins, their chemical composition is usually entirely different.

Over sixty years ago Adolph von Baeyer¹ showed that the reaction between phenols and aldehydes is a perfectly general one, and from the condensation of acetaldehyde and phenol in the presence of sulphuric acid as condensing agent he obtained a white sticky substance. Kleeberg² studied the condensation products of formaldehyde and phenol in the presence of hydrochloric acid. These he found difficult to identify, and alkaline reagents were without action on them. Further, his products were porous and when produced he could do nothing with them. A. Smith,³ realizing that Kleeberg's method would not lead to production of a moulding material capable of giving a homogeneous article, tried to moderate the reaction by the use of solvents which were afterwards removed at 100°. The removal of the solvents proved a formidable task, and what Smith got was a hardened mass in sheets or slabs unsuited to accurate moulding. Lüft⁴ tried to overcome the difficulty by adding solvent after partial completion of the main reaction, but the product was relatively brittle, and though it softened when heated, did not melt.

L. Blumer⁵ was the first to publish an account of the attempts to utilize the phenol-formaldehyde reaction commercially for making a shellac substitute. Using acid catalysts, such as the organic oxyacids, e.g. tartaric acid, he also showed that mechanical operations play a part in determining the properties of the resin. His soluble synthetic resins could be repeatedly melted and were moderate substitutes for shellac. A further step was taken by H. Story,⁶ who discontinued the use of condensing agents and also of solvents, and produced an infusible and insoluble product; slow hardening took place by drying at 80°, but Story's product came midway in properties betwixt the fusible and soluble resins, and those that were infusible and insoluble.

Next followed the classic paper of Dr. L. H. Baekeland⁷ in 1909 entitled 'The Synthesis, Constitution and Uses of Bakelite'. Herein was reviewed, as above, the attempts of his predecessors in this field of research. In his work he proved that temperatures considerably in excess of 100° were indispensable for the complete and rapid transformation of phenol-formaldehyde condensation products into the final infusible, insoluble product of the desirable properties associated with what is now the familiar synthetic material bakelite. This material may be taken as typical of the chemical substance

produced by the interaction of two common and important raw materials—phenol or carbolic acid (a coal-tar derivative) and formaldehyde (a wood-distillation product, now largely produced synthetically). Under specified chemical control, the phenol and the aldehyde combine to form an inert, solid body, generally devoid of odour, having well-characterized properties.

Baekeland's original master patent was filed in America in 1907, and on this were founded all the patents subsequently granted in most of the commercial countries of the world. This patented process, as H. V. Potter⁹ emphasizes in a résumé of this early pioneering work, differed from all previous ones in that it required a small amount of alkali such as ammonia to control the reaction. Other inventors had used large amounts of acid or had dispensed with an accelerator. The practical effect of Baekeland's discovery was that the differences between a controlled reaction and a non-controlled one opened the way to successful commercialization of the synthetic resin industry.

Baekeland found that acid condensation agents favour the formation of the fusible type of synthetic resins—the novolak type. These melt and resolidify after cooling, are soluble in alcohol, acetone, and other organic solvents, and possess properties making them substitutes for natural resins, though somewhat indifferent ones, in the varnish and lacquer industries. The products synthesized by Blumer, De Laire, and Thurlow belong to this first class. Baekeland found the use of bases favoured the formation of those products insoluble and infusible in their final form. To this second class belong the products made by Smith, Lüft, Story, and Knoll. Broadly speaking, Baekeland described these bodies in the second class as infusible, resinous substances: none of them can be retransformed into resins of the first class, though he showed that members of the first class could be transformed into those of the second.

The novel property of these resinous substances, as Potter points out, is that they readily flux or melt on heating, but if the heating be continued for several minutes the resinoids are chemically changed by the process of polymerization into hard non-fusible, amber-like masses, which have good insulating properties and are unattacked by solvents and most dilute acids.

Synthetic resins in the second class have properties making them of great use as moulding materials in the electrical, radio, and automobile industries; in the manufacture of such familiar articles as fuse handles and covers, radio parts, and insulators of all kinds; fancy goods like cigarette holders, cases, and ash trays; coloured beads, unbreakable cups and saucers, ornaments, and the like; as lining material for chemical plant; and for making moulded furniture.

Some of the so-called condensation products of formaldehyde and phenols are soluble in water, others are crystalline, and yet others are amorphous and resin-like. Among the latter some are easily fusible and soluble in alcohol and similar solvents, while others of this class are totally insoluble and infusible. It was the last-named

which Baekeland's work specially developed. Failure to appreciate the importance of temperature in the condensation reaction he thought was the reason his predecessors in this field of work did not succeed in producing desirable moulding materials. Moreover, he found that only small amounts of condensing agents were necessary; less than one-fifth of the amount which would be required to transform phenol into the phenolate.

Three distinct phases are involved in the reaction: (1) formation of the so-called initial condensation product which is designated *A*; (2) formation of a so-called intermediate product designated *B*; (3) formation of a final condensation product *C*. Phase *A* at ordinary temperature may be liquid, or viscous, or solid, and is soluble in ordinary organic solvents and in caustic soda solution. Solid forms of *A* are brittle and melt when heated. All varieties of phase *A* heated long enough pass into phase *B* and finally to *C*. Phase *B* is solid at all temperatures, brittle, and slightly harder than the solid form of *A* at ordinary temperature. It is insoluble in all the usual solvents. If heated it does not melt, but softens, becomes elastic, and on cooling is again hard and brittle. Appropriate conditions of heating convert it to the *C* form. Although the *B* form is infusible it can be moulded under pressure in hot moulds to a homogeneous coherent mass and the latter changed into the *C* form by the proper application of heat.

The *C* form is infusible, insoluble in all solvents, and indifferent to acids and alkalis. Of great strength and hardness, it does not soften to any serious extent when heated, and withstands temperatures up to 300°, above which it chars, but without fusion. It is a bad conductor of heat and electricity. The preparation of these condensation products *A* and *B* and their ultimate transformation into *C* for technical purposes constitute the so-called "Bakelite process"; to quote from Baekeland's paper. But while it is convenient to consider the bakelite reaction as taking place in stages, it is a more or less continuous process.

Despite Baekeland's discovery, varnish manufacturers were not disposed to consider the possibilities of synthetic resins, not even after K. Albert and L. Behrend⁹ introduced a modified, oil-soluble phenol-formaldehyde resin. Not, indeed, until the development of nitro-cellulose lacquers gave further impetus to research in synthetic resins was rapid and definite progress made. Broadly speaking, synthetic resins have been utilized as substitutes for shellac, rubber, asphalt and celluloid in the making of moulded articles, and as coating materials in place of shellac and varnish gums. The moulder and the varnish-maker are still the most important users, but this may not long be so: the synthetic resin industry is but in its infancy.

Between 1907 and 1910 Baekeland¹⁰ filed ten patents, yet prior to the filing of his first, in 1907, the only materials available for moulding were such natural products as shellac, rubber, bituminous materials such as asphalt and gilsonite, artificially produced materials as exemplified by ebonite and vulcanite, celluloid and xylonite, and

residual pitches from coal-tar, petroleum, and fatty acids. These artificially prepared substances—celluloid, ebonite, pitch—were, indeed, the pioneers of the synthetic plastics. But none of the foregoing is resistant to heat, none has great mechanical strength, and, being readily soluble in many of the usual industrial solvents, none has much stability. The inherent defect of these older plastic materials is that they are *thermoplastic*, a defect from which the newer plastics due to Baekeland are free.

Any broad view of the plastic industries shows how very old and comprehensive they are. The manufacture of pottery and earthenware depends on the plasticity of clay—a property with which man has been familiar from antiquity. Glass-making, the use of cement, putty, plaster of Paris, and asphaltic road-making materials are all dependent on plasticity; all are comprised in any broad survey of the plastic industries. Rubber is probably the best known of the plastic materials: 1,073,000 long tons are produced annually (1937-9) for the manufacture of automobile tyres, for electrical insulation work, for the manufacture of hoses, and for such hard rubber derivatives as ebonite and vulcanite. Paint and varnish, even, come within the orbit of this broad survey, as the ability of dried paint and varnish films to withstand, on exposure, considerable changes of temperature is dependent on their plasticity. Yet for reasons which should be apparent, none of the foregoing materials is included in this present survey.

In the pages following, therefore, a plastic material is understood as one which is solid at ordinary temperatures and allows of appreciable and permanent change of form without losing its coherence when subjected to mechanical stress. Plastic materials must possess, therefore, both elasticity and rigidity.

Difficult as is the task of giving a close definition of a resin, meaning thereby a natural resin, that of defining the term synthetic resin is still more difficult. But it may be considered as a complex, amorphous organic solid or semi-solid material, usually a mixture of substances. It is built up by chemical reaction and, in respect of its lustre, fracture, and comparative brittleness at ordinary temperature, closely simulates the natural resins. Insolubility in water, fusibility when heated, or plasticity when heated and subjected to pressure are other characteristics in which a synthetic resin resembles the natural resins. But in chemical constitution there is a wide divergence between the natural and synthetic resins, and equally wide is their divergence in the response they make to chemical reagents.

About the time Baekeland was carrying out his pioneering work on bakelite and similar synthetic resins, Redman and Aylesworth independently began the manufacture of two closely allied materials in the United States and litigation appeared imminent in 1916, but fortunately for the future well-being of the new industry, the interests of Baekeland and Redman were merged in the Bakelite Corporation, and their joint efforts then sponsored much of the early development work in that country.

A summarized account of much of this early development work on phenol-formaldehyde resinous products has been written by A. J. Buck.¹¹

The introduction of synthetic resins has caused most spectacular developments in the plastics and mouldings industries in the past twenty years. Many mouldings made from synthetic resins are unaffected by heat and moisture, are completely resistant to the action of solvents, and have great mechanical strength and excellent electrical properties. Further, these synthetic resins can be moulded into objects of beautiful shape, strong, durable, and convenient in use, capable of taking a great range of colour. The moulding material can be fabricated in the form of slabs, sheeted by calendering, extruded as rods and tubes, and subsequently cut into sizes suitable, after machine-tooling, for use in a variety of manufactures. It is now, indeed, definitely recognized as a new structural material of enormous value in architectural and interior decorating and furnishings.

By controlling the reaction, intermediate products both fusible and soluble are obtained, and it is in the conversion of these by heat into the final infusible form that one obtains material which forms the basis of the modern plastics industry. Baekeland showed that by mixing these intermediate resins with suitable fillers such as fibrous materials like asbestos, cotton flock, wood meal, and powdered ones such as mica, slate dust, talc, and barytes, a powder was obtained which could be filled into the moulds of heated presses. Under the influence of heat and pressure, the resin liquefies and with the filler bonds together into the infusible form under the continued influence of the heat and pressure. Finally, from the press is obtained in a few minutes the finished moulded article, of great mechanical strength, good electrical properties, wholly unaffected by temperature changes, moisture, or solvents.

Increasing scarcity of such natural decorative materials as amber, ivory, jet, tortoiseshell, &c., coupled with the advent of bakelite moulding materials and the fact that since 1918 it has been possible to use synthetic resins as plastic materials for the electrical industries, in place of the natural resins previously used in these trades, all combined to stimulate the production of new plastics and synthetic resins.

Raw Materials for Plastics. To produce a resin with commercial possibilities relatively cheap materials must be used, such as phenol, urea, formaldehyde, glycerol, phthalic anhydride, rubber, acetylene, and petroleum products, to name the more important ones. When other raw materials, available in abundant supply, become suitable the industry may take on other and more important developments than those which are at present its main support.

Dealing with raw materials in relation to the industry, H. V. Potter⁸ some time ago indicated the general availability of most of the essential raw materials required, if not all within this country, at least within the Empire.

G. J. Esselen and F. S. Bacon,¹² discussing the same topic, divide plastics into two groups: (a) those derived from coal-tar sources, and (b) those from non-coal-tar sources. In the latter group are petroleum, natural gas, acetylene on the one hand, and cellulose and plant products on the other. An enormous number of intermediate products is concerned, but phenol, phthalic anhydride, urea, ethylene, acetylene, formaldehyde are the primary materials.

How important coal is as a source of so many industrially important organic chemicals on which the plastics and synthetic resin industries are dependent is well reviewed in *Plastics and Coal* by N. J. L. Megson and K. W. Pepper.¹³ The relationship between many of the derivatives of coal and the finished resins is shown instructively arranged in a table (cf. p. 8).

Recently P. K. Frolich¹⁴ has listed the plastics and resins now manufactured, wholly or in part, from petroleum products or for which the petroleum industry should be able to supply the raw materials. The United States is a particularly good field for the necessary materials (cf. p. 320).

A. V. Grosse, J. C. Morrell, and J. M. Mavity¹⁵ also describe the catalytic dehydrogenation of mono-olefines to di-olefines, e.g. 1,3-butadiene, isoprene, piperylene, as sources of raw materials for resins.

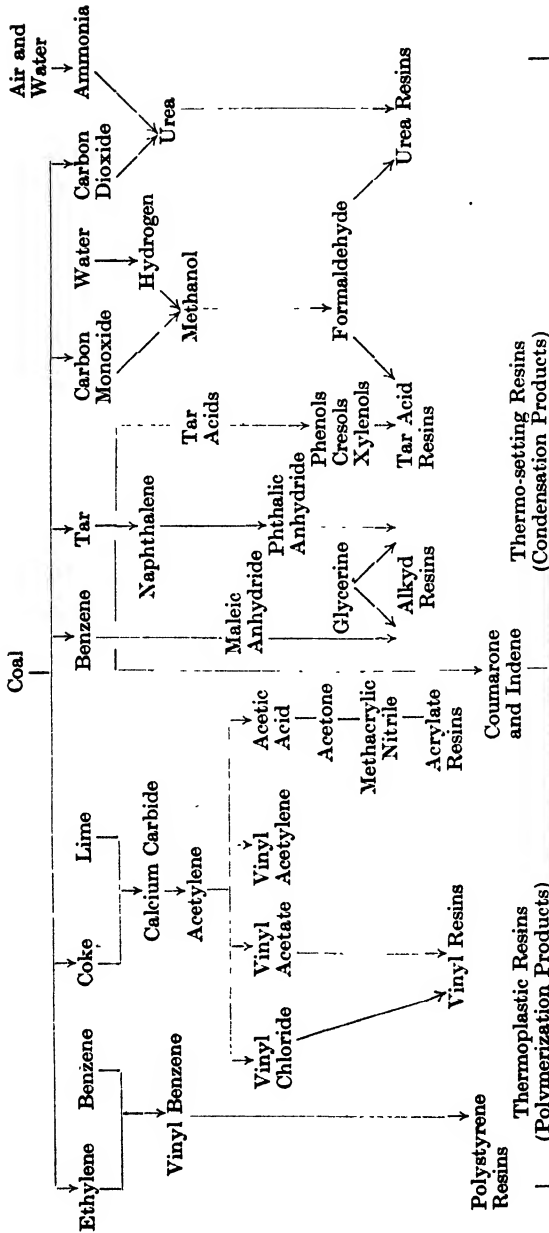
Plastic materials coming within the scope of this volume are of two main types—*thermo-hardening* and *thermoplastic*, respectively. Phenol-formaldehyde and urea-formaldehyde resins are of the thermo-hardening type. The chemical reaction involved in their preparation is not completed in the production of the moulding powders. In this form they are thermoplastic and may by application of heat and pressure be readily compressed in a mould to any desired shape. When the heated mould is at the required temperature the chemical reaction is then, and only then, completed, and an infusible product obtained. Thermoplastic materials are best exemplified by cellulose acetate, cellulose nitrate, and shellac.* These may be formed and reformed many times into definite shapes by the application of heat and pressure, providing sufficient plasticizing materials be incorporated to impart the proper flow. No chemical action occurs during the heating, and the materials remain plastic so long as the requisite temperature is maintained. Vinylite resins belong to this class also: they are inherently thermoplastic and remain so without the necessity of incorporating plasticizers. To be utilized in moulding operations, thermoplastic materials are heated to their softening point, pressure applied, the mould cooled, and the finished casting removed when set.

There are other types such as those which harden at a relatively low temperature and those which harden by chemical treatment. In this last grade the change from soft rubber to vulcanite is an outstanding example.

A convenient practical classification of the synthetic resins and

* Shellac has also thermo-hardening properties.

GENERAL INTRODUCTION



From U.S. Tariff Commission Report No. 131, *Synthetic Resins*, with Coumarone and Indene added.

allied plastics, not all of which, however, are fully considered in the present volume, is the following:

1. *Shellac and Natural Resin Types*. Rosin (colophony), copals, damars, kauri, accroides, lac (shellac).
2. *Bituminous Materials*. Natural asphalts, solid natural bitumens, such as glance pitch, gilsonite, and rafaelite. Manufactured residual pitches such as those from tars, petroleum, and fatty acids.
3. *Synthetic Resins Proper*. A number of subdivisions is desirable here, and the following seem the most suitable: (a) Phenol-formaldehyde types. (b) Furfural types. (c) Urea and thio-urea resins. (d) Glyptals and other polyhydric alcohol-polybasic acid types. (e) Coumarone and indene resins. (f) Vinyl, styrene, and other polymerization resins based on the $-\text{CH}=\text{CH}_2$ grouping. (g) Acrolein resins and the orca type. (h) Aldehyde-ketone condensation resins. (i) Petroleum resins. (j) Chlorinated compounds as resins. (k) Resins from sulphur and its compounds. (l) Resins from acetylene. (m) Miscellaneous resins.
4. *Ester Gums*. Hardened rosin and rosin esters.
5. *Protein Plastics*. From milk casein, and from soya bean.
6. *Cellulose Esters and Ethers*. Nitro-cellulose and celluloid. Cellulose acetate for mouldings, varnish films, &c. Ethyl cellulose, benzyl cellulose, and their allied and derived products.
7. *Rubber Derivatives*. Ebonite, vulcanite. Chlorinated rubber.
8. *Glues and Gelatines*. By-products of the industries dealing with bones and animal tissues.

For consideration of shellac and natural resin types, the reader is referred to the standard works on this section, in particular *Natural Varnish Resins*, by T. Hedley Barry (E. Benn, Ltd., London, 1932), also to the Technical Papers and Bulletins of the Shellac Research Bureaux controlled by the Indian Lac Cess Committee and the Shellac Research Bureau of the Polytechnic Institute of Brooklyn (U.S.A.). Apart from the use of shellac in the gramophone industry, natural resins do not find much use in the plastic moulding industries, while their use in the varnish and lacquer industries is outside the scope of the present volume.

In its distinct thermal hardening properties shellac differs from all other natural varnish resins; in addition, shellac possesses a tenacity and resiliency of its own, unmatched by any other material, natural or synthetic, at present known. Collectively these properties make it of special value in the gramophone industry, in the manufacture of bonded mica insulators, in electrical insulators in general, and in bonded paper tubes, &c.

A. J. Gibson¹⁶ has summarized recent work on heat treatment of lac leading to the production of a hard lac resin suitable as a new moulding material. Actually articles were made from cast shellac

from earliest times. The behaviour of this hard lac resin with accelerators and retarders, and with urea, is described.

Bituminous materials in use as moulding materials, as plastic coatings for cable masses, and as protective coatings for insulating purposes generally in the electrical industries, are of great importance, but the reader is referred to the well-known works dealing with bitumens for a proper treatment of the subject, and to an article on gilsonite by F. R. Jones.¹⁷

Synthetic Resins.

Since the establishment of the synthetic resin industry some few years ago, two parallel lines of development have been followed.¹⁸ On the chemical side new and improved resins have been prepared by variations in the purity of the reactants, by the use of such new reactants as urea, thio-urea, furfural, coumarone, indene, phthalic anhydride, and a host of other materials. Improved technique in moulding has followed engineering developments leading to the perfection of automatic presses and the introduction of injection moulding methods. Advances in the art of fabricating plastics have led to new applications.

Two broad types of chemical reaction are involved in the production of synthetic resins: (a) condensation, in which essentially new molecules are formed by interaction of two or more different compounds; (b) polymerization, in which the molecules of a compound react with each other to form a new compound. In some cases both types are involved, as in the phenol-formaldehyde, urea-formaldehyde reactions.

A broader general classification of the synthetic resins than indicated in the subdivisions given on p. 9 is that suggested by R. H. Kienle,¹⁹ namely:

I. *Heat-convertible resins*. Here the application of heat leads to the completely infusible and insoluble product, the chemical changes involved being irreversible. Phenol-formaldehyde resins of the bakelite type, urea-formaldehyde resins, and polymerization resins of the olefine and acetylene series are notable examples. II. *Heat non-convertible resins*. Heat causes little or no change in solubility or fusibility in these resins, the most striking of which are phenol-formaldehyde resins of the novolak type. III. *Element-convertible resins*. This is a miscellaneous group in which the development of the insoluble resin is effected by the intervention of extraneous elements such as oxygen. Resins of the glycerol unsaturated ester type are examples of this broad class.

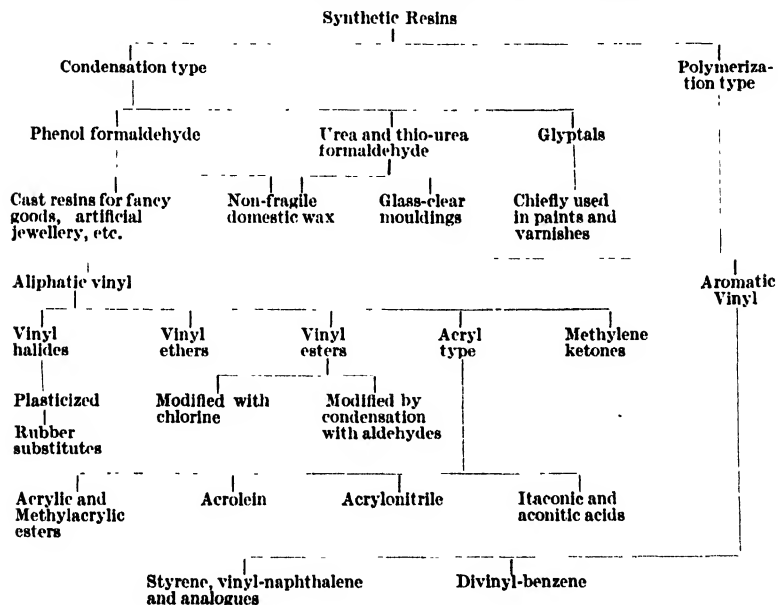
A classification on the above lines is proposed by G. T. Morgan, N. J. L. Megson, and E. L. Holmes²⁰ who describe the two classes as follows:

Condensation resins possess the characteristic property of hardening to yield insoluble, infusible masses, particularly under pressure, a property utilized in industrial moulding practice. They are thermo-

hardening and after hardening they possess comparatively high resistance to heat, and do not deform at moderate temperatures, but char at about 300°. Darkening of colour in cast resins can in general only be avoided by using prolonged heating at lower temperatures during the hardening process.

Polymerization resins: Products of this class made from substances containing only one $\text{CH}_2=\text{C}$ grouping remain fusible and soluble under heat treatment and are 'thermoplastic'. They may frequently be depolymerized by heating. They are generally pale in colour, and resemble glass more closely than do the condensation resins. Varieties of condensation and polymerization resins not included below are at present of less technical importance, e.g. sulphonamide resins, petroleum hydrocarbon resins, and furfural resins. The ester gums used in varnishes and derived from natural resins must also be included.

Classification of the Commoner Synthetic Resins

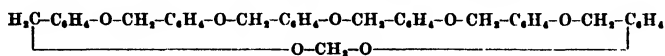


(a) **Phenol-formaldehyde resins.** The early success which attended the introduction of the first phenol-formaldehyde resins led to an intensive study of most of the known phenols, cresols, and aldehydes, and from the many combinations which were tried a great variety of resins resulted. But for ordinary commercial hot-moulding practice, in which rapidity of hardening is of prime importance, the products derived from the simpler phenols and formaldehyde have

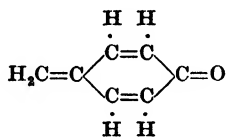
proved unrivalled. Baekeland differentiated commercial phenol-formaldehyde condensation products according to their behaviour when heated into (1) resinoids, the heat-hardening type, (2) novolaks, the permanently fusible type, and later simply resins by reason of their similarity in behaviour to the natural resins.

Allen, Meharg, and Schmidt²¹ have recently summarized the chemical reactions involved in the formation of synthetic resins, particularly as applied to the outstanding types of synthetic varnish resins with which one is now familiar.

Baekeland^{7, 22} tentatively suggested the formula

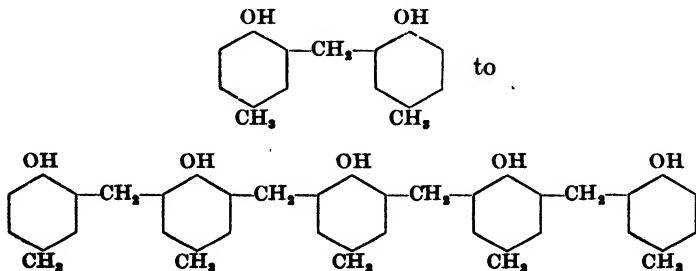


This was modified by Raschig²³ and later by Blumfeldt.²⁴ Wohl,²⁵ after studying acrolein derivatives of phenols and the so-called resorcin ethers, advanced the hypothesis that these resins are polymerization products of methylene derivatives of the tautomeric phenol



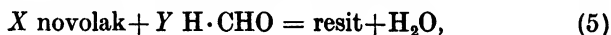
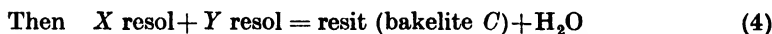
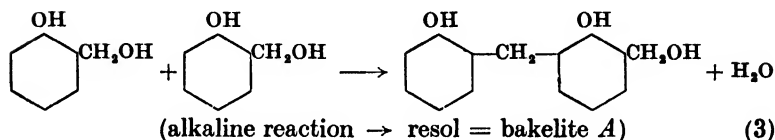
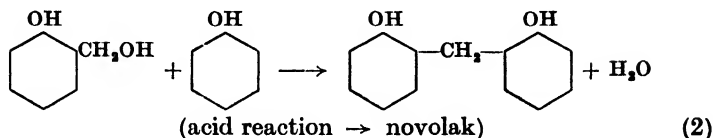
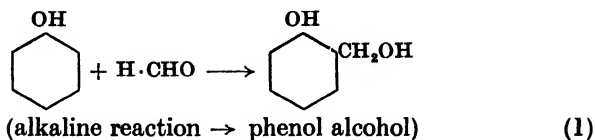
Megson and Drummond^{26, 27} tried to isolate intermediate products in the synthesis, and Koebner,²⁸ studying the *p*-cresol-formaldehyde condensation, concluded that acid-catalysed, permanently fusible cresol-formaldehyde resins (novolaks) are mixtures of bi-, tri-, tetra-, and poly-nuclear compounds. The hydroxyl groups of the poly-nuclear compounds are unchanged and are with difficulty soluble in dilute alkalis owing to their formation.

Their resinous character is due to a mixture of innumerable isomers and the variety of large and often complex molecules present. Koebner²⁸ synthesized compounds varying from those with bi-nuclear structure to those with penta-nuclear, viz.:



A great variety of reactions is possible according as acid, alkaline,

or neutral catalyst is used, and he set out the following as illustrative:



Equation (2) represents the formation of the simplest novolak, and (3) represents the simplest resol (bakelite A). In equation (2) 1 molecular proportion of phenol reacts with $\frac{1}{2}$ molecular proportion of formaldehyde. As the ratio approaches 1:1 the molecular chains, which constitute the novolak, lengthen, resulting in a resin of higher melting-point, lower solubility in alcohol or caustic alkali. When the limit of 1 molecule phenol to 1 molecule of formaldehyde in the resin is reached, the stage of finality characterized by infusibility and mouldability is reached.

F. Pollak and F. Riesenfeld,²⁹ from a study of the 'novolak', or acid-catalysed reaction between phenol and β -polyoxymethylene, consider it to be constituted of a chain of 7 molecules of phenol with 6 of formaldehyde, the 2 end phenol residues differing from the remaining 5 in being disubstituted instead of trisubstituted. Using alkaline conditions, on the other hand, H. Stäger³⁰ has investigated the products of reaction between formaldehyde and phenol, cresols, and phenol-cresol mixtures and finds that the chemical properties, e.g. loss in weight on thermal hardening, content of volatile products, and the bromine absorption and molecular weight of the benzene soluble fraction of the volatile products are insufficient to characterize the resins. From the electrical properties of the hardened resins on which the effect of the phenol is very marked, it is concluded that an essential difference between phenol- and cresol-formaldehyde resins lies in the lower degree of polymerization under similar

conditions, and consequently more pronounced polar characteristics, in the former.

Meyer and Mark³¹ point out that the tendency towards interlocking chains and 3-dimensional structures is easily possible in reactions between phenol and formaldehyde. If for phenol be substituted *o*- or *p*-cresol, in which the relative position is blocked by a CH₃ group, the resulting products are not so high in molecular weight nor so insoluble: the resultant compounds belong more to the chain polymer type of compound. Taken in all, the available evidence points to polymerization as the cause of resin formation in the foregoing types.

The early difficulty experienced with the synthetic resins in incorporating them with the drying oils was a serious handicap to their use in the varnish industry. But research in recent years has succeeded in producing types of resins freely compatible with the drying oils and usual varnish vehicles. The first successful patent for converting phenol-formaldehyde resins into oil-soluble resins was that due to Albert and Behrend.⁹ Resins of this type were named Albertols and they can replace many of the natural gums usually employed in the varnish industry; in fact Albert and Behrend³² now claim that these products are as satisfactory as many natural resins in oil varnishes. Several grades are now made, and they are soluble in benzene, solvent naphtha, and carbon tetrachloride without difficulty. Oil-soluble resins have been obtained from some higher phenols, e.g. *p*-tert.-amylphenol or *m*-xylenol, from lignite tar oils and from a variety of aromatic ethers and allied bodies by use of appropriate condensing agents. Oil-soluble resins of the Albertol (or Amberol) type are also made from monocyclic ketone condensation products, from some of the glyptal resins and from some of the coumarone resins, as well as from the phenol-formaldehyde types originally used by Albert and Behrend (cf. Chapter IX).

(*b*) **Furfural resins** (cf. Chapter XIII). Furfural (furfuraldehyde or furol). C₄H₃O·CHO, a colourless oil obtained from pentoses by distilling them with concentrated acids, has all the properties of an aldehyde, can yield condensation products, and is able to replace formaldehyde in a number of synthetic resins. Furfural was first made in appreciable amount by Stenhouse³³ from sawdust and oatmeal by treatment with sulphuric acid, but it was not until the introduction of a cheap method of making furfural from oat hulls in the United States in recent years that any great industrial prospect arose for derivatives of this aldehyde. A. J. Hammer³⁴ has described the development, from which it appears that the process yields 20 per cent. furfural from the hulls, a 50 per cent. efficiency being achieved, and the resultant aldehyde is of 98–99 per cent. purity.

Commercially the reaction between furfural and phenols takes place in the presence of alkaline catalysts, dark insoluble resins resulting. Actually furfural resinifies in the presence of hot alkali to give a similar type of product. The early resins of this type were too dark for use in varnishes, though they found application in the

making of cold-moulding materials. Since their introduction extensive investigations into their properties and uses have been made, and they are now produced as condensation products of many diverse classes of compounds. They find use as plastic materials in the varnish and coating industries and have been made compatible with tung oil. Recent progress in this field has been described by E. E. Novotny and F. N. Peters³⁵ in a series of papers.

(c) **Urea and thio-urea formaldehyde resins** (cf. Chapters IV and X). Early attempts fifty years ago to condense formaldehyde and urea aroused no interest. Cheap methods of synthesizing urea from ammonia and carbon dioxide under pressure, and of converting calcium cyanamide by ammonia and sulphuretted hydrogen into thio-urea, as recently described by K. M. Chance,³⁶ have stimulated the production of the resins described under this heading.

H. John took out the first patent in 1920,³⁷ used no condensing agents, and got three stages in the formation of resins: *A* a soluble stage, *B* an insoluble, jelly-like stage, *C* a hardened, solid stage. F. Pollak³³ and his colleagues took out a number of patents, used a variety of condensing agents, and among the diverse products they got was one named 'Pollopas'—a transparent, colourless solid resembling rock crystal.

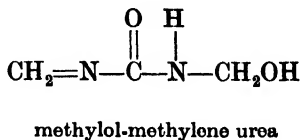
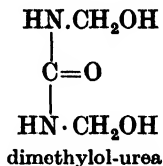
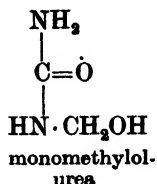
Linking of the urea molecule probably takes place in stages, water-soluble methylol-ureas being formed: these give solutions which may be adhesive. These link with other molecules, and as the molecular system increases resinous characters develop. Then the resin becomes less soluble as size continues to grow. Finally, the solubility disappears and a hardened resin, as clear as glass, is the final stage.

The *A* stage is soluble in water and is useful for impregnating paper and other fabrics which can be hardened by heat. Incorporated with fillers and pigments, they are used as moulding materials. The *B* stage of the resin is jelly-like, but cools to an elastic insoluble substance. This can be ground to powder and under heat and pressure passes into the *C* stage resin. K. M. Chance³⁹ has described the developments made in manufacture of the two types of aminoplastic powder on the market in 1934; one a straight urea powder, the other being a product of urea and thio-urea.

The amino-plastics, of which urea and thio-urea resins are the principal ones, have properties making them suitable for the production of domestic articles. They can be produced white, or in bright, attractive colours, and their light resistance is good and they are thus able to compete with the brightly coloured and non-translucent grades of bakelite, though not with the black or brown grades. As 'Beetle' ware,⁴⁰ the urea plastics have made great headway, as in moulded form they are free from taste and odour.

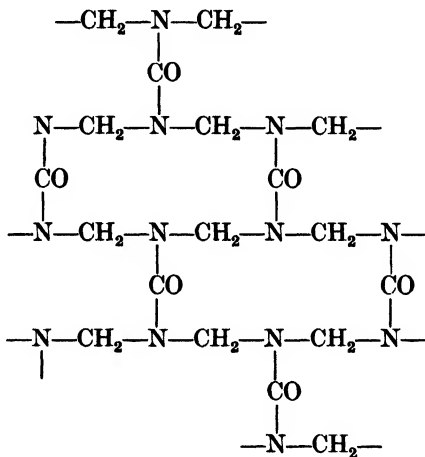
Their exact constitution is not known, but McMaster⁴¹ has succeeded in isolating —C—N— ring compounds similar in structure to those formed when benzene sulphonamide is condensed with formaldehyde. Walter and Glück⁴² studied these resins in connexion with the general problem of hardening and have isolated a crystalline di-

methylene-methylol-tri-*o*-toluene-sulphonamide. Such intermediate products as



&c., have also been isolated.

T. S. Hodgins and A. G. Hovey⁴³ believe the structure of the urea resins is best represented by a formula such as:



Urea resins are used to render textile fabrics non-creasing, to prevent shrinkage, and to prevent felting of wool. The Calico Printers' Association,⁴⁴ and Tootal, Broadhurst & Lee,⁴⁵ have taken out numerous patents protecting the use of urea and other resins for use in the textile industry. R. V. V. Nichols and P. Larose⁴⁶ have given a résumé of some recent developments in this field of work which is now extended to include a great variety of resins in addition to the urea-formaldehyde type. J. Warwick⁴⁷ also discusses the uses of urea resins in anti-crease treatment.

(d) **Glyptal (alkyd) type resins** (cf. Chapter XI). Polyhydric alcohols and polybasic acids condense to form resins, the typical member of the group being formed from glycerol and phthalic anhydride, thereby conferring the name Glyptals on members of the group. van Bemmelen⁴⁸ as far back as 1856 studied the reaction between glycerol and such acids as succinic and citric. Lourenço⁴⁹ observed the transformation of the water-soluble, sticky product

obtained by the reaction at 160° into hard, insoluble substances by heating at 215°. Watson Smith⁵⁰ got a product by the reaction of glycerol and phthalic acid, and this he thought to be a glyceride of phthalic acid: the product was hard and glassy. Only when the commercial production of cheap phthalic anhydride became possible due to the work of C. R. Downs,⁵¹ H. D. Gibbs,⁵² and others, followed by the cheap production of such acids as succinic, maleic, fumaric, and benzoic, did the production of glyptals make definite headway. C. R. Downs⁵³ has described the manufacture of phthalic anhydride by the vapour-phase catalytic oxidation of naphthalene.

These resins, known also as the alkyd resins, and sold as Glyptals, Resyls, Paranol, Paralac, Alkydals, and Dulux resins, &c., are now available in both fusible and infusible form, and thus find use in many branches of the electrical, varnish and lacquer industries as well as in the moulding trades.

A. G. Hovey⁵⁴ has described the application of the fusible alkyd resins as bonding materials for almost every variety of organic and inorganic materials. Their tackiness is their outstanding property, added to which is their high degree of penetration into fibrous material. Alkyd resins were first used in the manufacture of composite mica articles where good insulation is essential. They may be dissolved and utilized as solutions for building up micanite as insulation for use in the electrical industry.

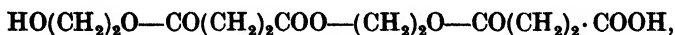
These resins may be converted into rosin-modified forms for varnish gum substitutes. Replacement of part of the dibasic acids by monobasic acids makes possible the production of other varnish and lacquer resins of high weathering-properties; tough, elastic films immune to shock result from such resins. Extensive use has been made of alkyd resins as a base for paints and enamels on account of their good colour.

Carothers⁵⁵ and his associates, investigating the reactions involved, showed that esterification of dibasic acids and glycols leads to polymerization with the necessary structure unit



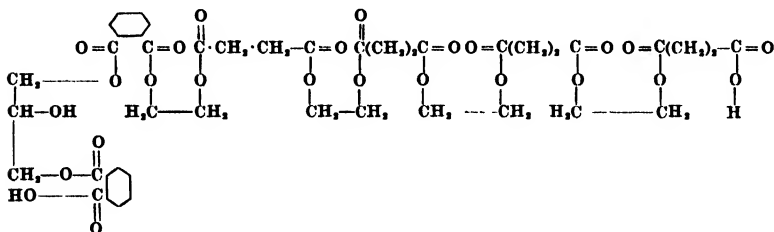
They further found that if the number of atoms in the unit chain be 5, the product is monomeric and cyclic: if the number be 6, the product may be monomeric or polymeric, but if the number be greater than 6, the product is exclusively polymeric.

The mechanism of the reaction in the alkyd resins is one of ester interchange, viz. 2 molecules of $HO(CH_2)_2O-CO-(CH_2)_2COOH$ unite to form



&c. The upper limit of molecular size is determined by physical considerations, e.g. increasing viscosity of the resins hinders diffusion of the volatile by-products and decreases the mobility of the reactants.

Kienle⁵⁶ studied the kinetics of this type of reaction and concluded that a chance locking of the molecules is a condition of the formation of resins of this class. Kienle and Schlingman⁵⁷ further applied this theory to the production of flexible, heat-convertible alkyd resins. Here the structure is assumed to be such that flexible, heat-convertible polymers are attached through primary valency linkage to heat-convertible resins.

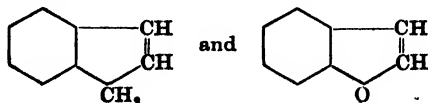


No actual chemical evidence exists to form a basis for a structural formula of the final infusible glyptal resins, but they may be tentatively portrayed as here shown.

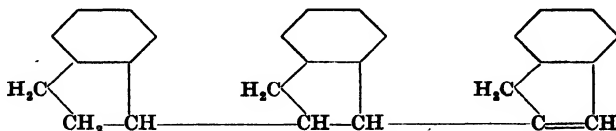
A type called 'Petrex' is made by recourse to the diene reaction utilizing certain terpenes and maleic anhydride. The formation of such resins is described by E. R. Littmann⁵⁸ as an industrial application of the Diels-Alder diene synthesis, i.e. a reaction between a C—C conjugated system and one containing a C—O conjugated system. These terpene-maleic anhydride resins tend to form peroxides which catalyse the polymerization of drying oils and hasten film formation (cf. Chapter XIII).

(e) **Coumarone and indene resins** (cf. Chapter VII). These are formed under appropriate catalytic influence, by polymerization of the coal-tar fractions coumarone and indene, respectively. These resins do not form infusible bodies and are therefore unsuited as moulding materials, though they may be incorporated with such with advantage in some cases. They find application in linoleum manufacture, and in the manufacture of rubber goods which require to be tacky, while the palest and hardest of them are used in varnish making. Being absolutely neutral they can be safely used in conjunction with basic pigments: these advantages and others from the viewpoint of the varnish industry have been indicated by T. Hedley Barry.⁵⁹

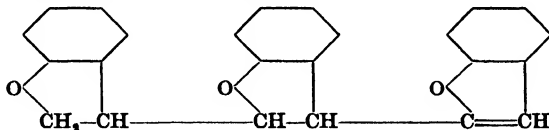
Indene, $C_8H_4 \cdot C_3H_4$, and coumarone, $C_8H_4 \cdot C_2H_2O$, are both colourless liquids of b.p. 182° and 172° respectively. They have long been known and are represented respectively by the formulae



According to Whitby and Katz,⁶⁰ the structure of *p*-indene is represented by the formula

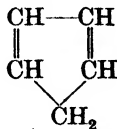


and *p*-coumarone is probably similar, viz.:



Such structures are in agreement with the chemical characters exhibited by indene and coumarone resins—great stability towards alkalis coupled with some susceptibility to oxidation.

Associated with them is cyclopentadiene represented by the formula



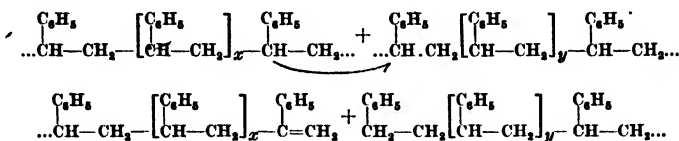
All three are found together in distillation fractions of coal-tar, but the difficulty is their complete separation from the solvent naphtha in which they occur. Polymerization is usually carried out on fractions richer in one or other of the three.

H. Barron⁶¹ in a review of recent work on coumarone resins, which are tacitly assumed to embrace the mixtures of resins derived from coumarone, indene, and cyclopentadiene, considers it doubtful if there are any cheaper synthetic resins than these. They are widely used in U.S.A. and Germany and range from thick, dark, semi-fluid resins to clear, very hard solids.

(*f*) **Styrene and vinyl resins** (cf. Chapter V). Though not so much recognized in the varnish industry as the phenol-formaldehyde and alkyd types, the vinyl and styrene resins are used in lacquers and in nitro-cellulose finishes. Both are thermoplastic and chemically inert, and can be moulded to clear, transparent, non-inflammable solids capable of compounding with fillers and taking colour. J. G. Davidson and H. B. McClure⁶² have described the commercial development of these resins for mouldings, and, according to C. Ellis,⁶³ styrene lends itself commercially to the production of light-coloured moulding and coating compositions known as 'Trolitul', 'Resoglaz', 'Victron'.

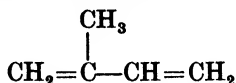
Berthelot⁶⁴ showed in 1851 that certain hydrocarbons passed through a red-hot tube gave styrene and indene, while S. F. Birch and E. N. Hague⁶⁵ obtained 5 per cent. styrene and 2 per cent. indene

by the pyrolysis of Persian natural gas. Styrene is $C_6H_5 \cdot CH=CH_2$ and according to Staudinger,⁶⁶ who has studied carefully its compounds, the polymerized styrene chain can be represented by the following scheme.



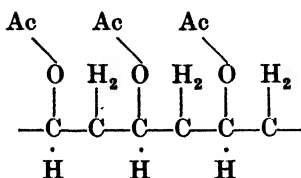
Here the hydrogen atom at the end of the chain has attached itself to the end of another molecule, so that the first chain now contains a free double linkage.

Vinyl compounds contain the grouping $CH_2=CH-$ present, for example, in isoprene, which is β -methyl divinyl:—

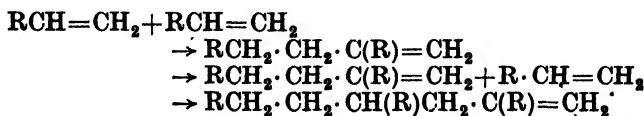


and in butadiene (divinyl) $CH_2=CH-CH=CH_2$. Polymerization of vinyl compounds has been known for a hundred years, but the pioneering work on the industrial application of vinyl polymers is due to O. Stromuizslenski,⁶⁷ who prepared vinyl chloride, while Klatté⁶⁸ discovered vinyl acetate. At the present time polyvinyl acetal resins under the names 'Alvar' and 'Formvar' are made by Shawinigan Chemicals Limited.⁶⁹

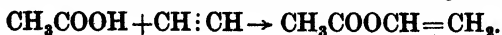
Vinyl acetate, $CH_3COOCH=CH_2$, is the chief material, either alone or with vinyl chloride, for the manufacture of the vinyl resins known as 'Vinylite', 'Mowilith', 'Vinnapas'. The structure of vinyl acetate is probably similar to that of the styrene polymers:—



Whitby and Katz⁶⁰ formulate the reaction which occurs as being along the following lines:



and in like manner for other vinyl polymerization products. S. N. Ushakov and J. M. Feinstein⁷⁰ described a vapour-phase method of synthesizing vinyl acetate based on the following reaction:



G. O. Curme and S. D. Douglas⁷¹ in a review of these vinyl chloride-vinyl acetate resins point out that in addition to properties already mentioned above, these resins are valuable on account of their strength and dielectric properties. Their resistance to water is an outstanding characteristic of vinylite resins, which are almost as effective against soaps, alkalis, oils, alcohols. Properties depend somewhat on the proportion of chloride to acetate; that with 85–88 per cent. vinyl chloride is best.

The question why monovinyl compounds of the type $\text{CH}_2=\text{CHX}$ polymerize while those of the type $\text{CH}_2\text{CH}=\text{CHX}$ do not, is not yet satisfactorily answered. Consequently it is the more surprising that substances like maleic acid can be induced to interpolymerize with styrene. J. B. Rust⁷² (of Ellis-Foster Company, U.S.A.) has described the results of such co-polymerization, the products of which depend on the catalyst used, temperature, and proportion of vinyl compound to the diethylene glycol maleate. Some are water-white resins and their greatest virtue lies in their rapidity of cure and their ability to be made either in light colours or water-white as may be desired (cf. Chapter XI).

S. D. Douglas⁷³ of Carbide and Carbon Chemicals Corporation, U.S.A., discusses the influence of chemical composition upon properties and uses of vinyl chloride and vinyl acetate co-polymers, and among important advances in these resins is their use in coating paper; some are suitable for injection moulding; others are used in making synthetic textiles. A plasticized form of polyvinyl chloride is used for coating wire around which it is extruded. It can be suitably pigmented and possesses advantages over rubber for insulation.

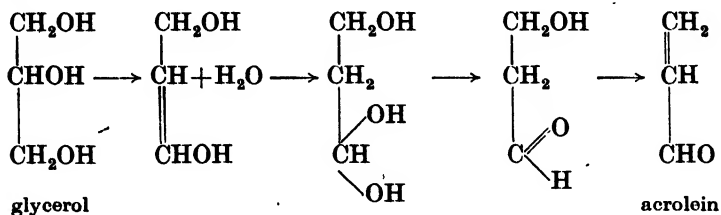
Vinylite resin-coated paper is used as a liner for various forms of closure, such as bottle-caps, &c.

(g) **Acrolein and acrylic acid resins** (cf. Chapter VI). The polymerization of aldehydes alone, particularly such as acrolein, acetaldehyde, &c., yields resins of industrial importance. McLeod⁷⁴ showed that even traces of alkali, weak or concentrated, converted acrolein quantitatively in the cold to a polymerized form. Moureu, Boutaric, and Dufraisse⁷⁵ worked out during the 1914–18 War a cheap method of making acrolein and stabilizing it. Pure acrolein polymerizes in the cold in presence of organic and inorganic bases, the polymerized product being a white powder of m.p. 80–100° soluble in most organic solvents, but insoluble in water. Acrolein condensed with phenol forms a hard moulding resin, suitable as an electrical insulating material, marketed under the name 'Orca'.

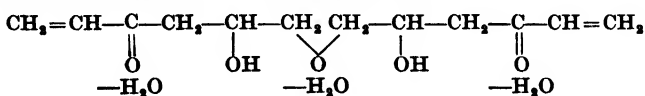
S. N. Ushakov and E. M. Obriadina⁷⁶ describe methods of obtaining resin-like products from glycerol by heating with easily reduced salts of sulphurous and sulphuric acids as catalysts. Products obtained by treatment of glycerol have no independent technical importance alone, but they impart elasticity to phenol resins without depriving the latter of their characteristic properties. The addition can be effected during the process of condensation. Glycerol resins should

be useful for preparation of different protective coatings, acid and alkali-resisting; glycerol resins can also be used as plasticizers for production of plastic masses of albuminous base (e.g. casein).

Data obtained suggest the following scheme of formation of these resins:



On the one hand, di- and tripolyglycerides are formed by separation of 2 or 3 molecules of glycerol. On the other hand, acrolein is formed by action of dehydrating agents on glycerol, and this in turn acts reciprocally with glycerol and polyglycerides



Further, the polymerization in the groups $\text{CH}_2=\text{CH}-$ is possible with the high molecular weight obtained. Polymers of acrolein and glycerol are in admixture. The polymerization products of the alkyl esters of alkyl acrylic acid are glass-like and can be machined and turned (Diakon). They can be used as a bond for safety glass and machined into objects rivalling glass in brilliance, toughness, and durability.⁷⁷

L. Klein and L. T. Pearce⁷⁸ describe the properties of acrylic acid derivatives, especially the Acryloids. These are neutral, can be used with any pigments; and make good films as they can be brushed, sprayed, or dipped. Though they will air-dry, it is best to bake them to ensure a hard, adhesive film of superior gloss.

H. T. Neher⁷⁹ points out that acrylic resins differ from other forms by reason of their transparency, great elasticity, adhesive qualities, and resistance to most reagents and solvents. Their brilliant, water-white transparency, high light-transmission, and high optical clarity, coupled with their remarkable stability to heat and light, make them of great value. Varying from the hard, tough methyl methacrylate to the soft, sticky polymers of the higher aliphatic acrylate, all have low water absorption not exceeding 3 per cent. Electrical resistance is good.

Both polyacrylates and poly-methacrylates are permanently thermoplastic and so are used as intermediates in laminated glass. Owing to their susceptibility to temperature changes, it is best to make these resins from a mixture of several monomeric forms. In U.S.A. a laminated safety glass 'Plexite' and on the continent

'Luglass' and 'Scyla' containing polyacrylic acid derivatives, are extensively made.

Transparent resins of polystyrene, vinyl, and methacrylate resins have been described in numerous recent patents.^{80,81,82} In Great Britain the methacrylate polymers predominate, and the acrylate varieties in U.S.A. Various types of organic glass are thus made: 'Plexiglas' in Germany, 'Pontalite' or 'Leucite' in U.S.A., and 'Perspex' and 'Diakon' in Great Britain; both the latter are made by the I.C.I.

M. Langley⁸³ has described the application of many of these new types in the manufacture of windscreens and windows in aircraft (cf. Chapters V and VI).

Owing to the inertness of methyl methacrylate plastics to the action of corrosive fluids a modified form is used as a denture material known as 'Kallodent', and during the last two and a half years 50,000 dentures have been made from it.

(h) **Aniline-benzaldehyde type of resins** (cf. Chapter XIII). The possibility of condensing amines and aldehydes has long been known, and a resin soluble in benzene and linseed oil can be formed from aniline and benzaldehyde with hydrochloric acid as the condensing agent. Rauch⁸⁴ has patented the manufacture of this resin.

According to K. Frey⁸⁵ resins of this type are much used in Switzerland. They do not soften below 150° and can be moulded without a filler to give brown, translucent objects of great strength.

Benzylaniline formaldehyde resin has been studied by Herzog:⁸⁶ a hard, brittle, transparent yellow resin soluble in cold benzene, but dissolved by turpentine only after heating. Aniline and formaldehyde condense in presence of traces of acid or alkali, and the resultant resin, patented by Böhler,⁸⁷ improves the solubility of natural resins.

(i) **Petroleum resins** (cf. Chapter XII). Petroleum resins from a number of unsaturated petroleum fractions have now reached the production stage. Treatment of these unsaturated fractions with aluminium chloride yields a brown, neutral resin soluble in drying oils to form varnishes which can be thinned with petroleum spirits. These resins actually accelerate the drying of tung oil and should be of service in all operations requiring tung oil.^{88,89}

It is well known that products of resinous character result from petroleum cracking, these resinous bodies being highly polymerized hydrocarbons. These interact with phenols to form synthetic resins akin to bakelite, and this method of utilization is patented by J. C. Morrell and G. Egloff.⁹⁰ The cracked petroleum distillates are passed, whether hot or cold, or in vapour form, through fuller's earth, bentonite, or other absorbent earth. The absorbed polymeric hydrocarbons are recovered by solvent extraction, and after removal of the solvent the hydrocarbons are mixed with phenols in equal proportions heated to 150° and oxidized by air or chlorine oxides until the mixture is suitably viscous.

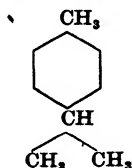
C. A. Thomas and F. J. Soday,⁹¹ in a paper mainly concerned with data on the dispersing and wetting properties of polymerized hydrocarbons and their relation to the paint and varnish industry, have examined the resins from highly cracked distillates arising during pyrolysis of hydrocarbons. With a wide range of cracking conditions a number of hydrocarbon resins with different characteristics can be obtained by varying the polymerizing conditions.

S. C. Fulton and A. H. Gleason⁹² describe with a summarized literature work on the production of resins and their condensation with formaldehyde, during cracking from both light and heavy distillates, and especially from those of high aromatic content.

(j) **Chlorinated compounds as resins** (cf. Chapter XIII). Chlorination of diphenyl ($C_6H_5 \cdot C_6H_5$) forms the so-called 'Aro-chlors' which range from colourless liquids to pale yellow, brittle resins. At present their main application is in fireproof coatings. Penning⁹³ has described these resins.

Geller⁹⁴ has patented the chlorinated products of paraffin wax: the properties and uses of these bodies are largely dependent on the extent to which chlorination has been carried. Those of lower than 70 per cent. chlorine content are soft and wax-like; that containing 70 per cent. chlorine is a hard, brittle, transparent resinous substance.

Low-temperature chlorination of cymene gives rise to resins insoluble in acids, alkalis, or ethyl alcohol. P. H. Groggins⁹⁵ has described the formation of these resins, which are suitable in coating



and insulating compositions but not as moulding materials as they do not form infusible bodies on application of heat and pressure.

(k) **Resins from sulphur and its derivatives** (cf. Chapter XIII). These have been produced in recent years, particularly in the United States. Some accounts of these developments which have appeared describe the production of plastic materials by condensing aniline, *o*-toluidine, α -naphthylamine, and other aromatic amines with sulphur or its chlorides. Products up to 40 per cent. sulphur content have been formed: these vary in tint from light yellow to brownish yellow, and they are soluble in acetone but not in alcohol. The tendency seems to be for greater insolubility to follow an increasing sulphur content.⁹⁶

In a patent due to W. C. Wilson⁹⁷ is described the combination of nitrobenzene and sulphur, and by adding asbestos as a filler a moulding powder is obtained.

As early as 1907 phenol-sulphur resins had been studied and the melting-point, hardness, and insolubility of such resins found to

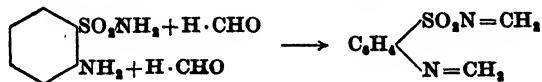
increase with increasing sulphur-content. Up to a temperature of 140° soluble resins are obtained, but heating to 180° leads to production of the insoluble form. These resins are soluble in such solvents as acetone, alcohol, ether, and alkalis, but insoluble in acids, and it has been proposed to use them as acid-resisting materials.

C. Ellis developed the condensation of sulphur monochloride and sulphur dichloride with phenol, cresols, and naphthols, and of the resultant products he finds that the cresol-sulphur resins are dissolved readily by linseed oil and so form a useful basis for varnish compositions. These resins are resistant to alkaline carbonates and soaps, but are attacked by nitric acid and strong caustic alkalis. A further advantage of these cresol resins is that they can be dyed, and from them can be produced acid-resisting coatings for wood-work.⁹⁶

A development which is awaited with interest is the condensation of definite fractions of tar acids or low-temperature tars with sulphur. G. T. Morgan and N. J. L. Megson⁹⁸ showed some time ago that the crude phenolic fractions from a typical low-temperature tar could be purified sufficiently to form phenol-formaldehyde resins. These resins, of the hardening type, were found the equal in electrical tests of good commercial resins made from pure phenol. Resins of the novolak type accompanied the hardening resins. Attempts are now being made to use such reasonably purified tar acids as Morgan and Megson obtained in order to form sulphur-resins. The possibilities of sulphur condensations with phenolic bodies like resorcinol, pyrogallol, and their congeners are being investigated also.

Thiokol⁹⁹ is a polyethylene sulphide formed from ethylene dichloride and an alkali polysulphide. This resin functions as a rubber substitute on account of its elastic rubber-like character and its general insolubility. Moulded plastics made from certain of these polyethylene sulphides offer the very highest resistance to the solvent action of mineral oils. Their odour is, however, a great drawback, and restricts their use to outdoor applications.

Sulphonamide Resins (cf. Chapter XIII). Resins of a fusible and soluble type result from the condensation of formaldehyde with aryl-monosulphonamides, whereas hard and infusible resins follow the condensation of formaldehyde with di- and trisulphonamides, e.g. aniline-sulphonamide with formaldehyde:



The most important use of these resins is in electrical insulators.

A renewal of interest has arisen in resins formed by condensing olefines with sulphur dioxide according to R. D. Snow and F. E. Frey,¹⁰⁰ who discuss the reactions at some length. These are stated to take place only in presence of a catalyst.

(l) **Acetylene as a source of resins** (cf. Chapter V). Herzog¹⁰¹ described the action of metallic catalysts such as copper on acetylene (C_2H_2), an insoluble, light brown, voluminous powder, 'Cuprene', being formed. This has been suggested as a filler in moulded articles and in linoleum paints.

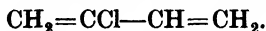
A number of acetylene derivatives have been used as sources of resinous materials, viz.:

acetylene, $CH:CH$

monovinyl acetylene, $HC:C-CH=CH_2$

divinyl acetylene, $CH_2=CH-C:C-CH=CH-CH=CH_2$.

Carothers, Williams, Collins, and Kirby¹⁰² converted monovinyl-acetylene by means of hydrochloric acid into chloroprene, and in turn polymerized this to Duprene, a substance very akin to natural rubber in respect of its physical properties. These are described also by Bridgwater.¹⁰³ Chloroprene is chlorodivinyl:—



Hayden¹⁰⁴ described the thickening by heat of divinyl acetylene. The product [S.D.O.] behaves like a drying oil and gradually hardens to a firm acid-resisting surface.

(m) **Miscellaneous resins** (cf. Chapter XIII). Commercial ground wood-pulp from hemlock and spruce as the raw material is now used as basis for plastic material.¹⁰⁵ Stoved in air to equilibrium moisture-content, with phenol or cresol and hydrochloric acid as condensing agent it yields a product, which after air-drying for 56 days, grinding and heating at 80° , develops plasticity and can be moulded under pressure. Baked to 150° the moulded plastic has electrical properties the equal of substances usually used and superior to asbestos. The material is not highly resistant to boiling water and is slightly brittle. Its use depends on the pentosans in wood and their ability to form resinous adhesives within the wood pulp, and these in turn serve to act as a binder for the rest of the wood pulp as the filler or inert material.

Sweeney¹⁰⁶ described the production of resinous condensation products from the pentosans in corn-stalks, and recently L. R. Jones¹⁰⁷ has patented their production from peanut-hulls. Low cost of production is the great advantage of all these resinous bodies.

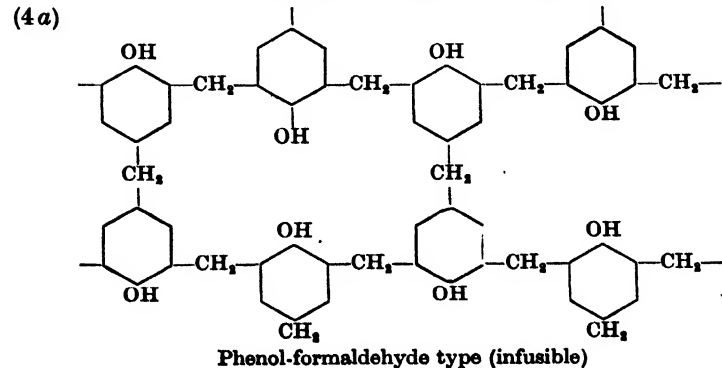
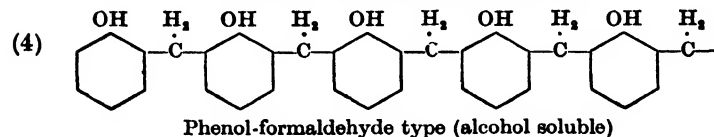
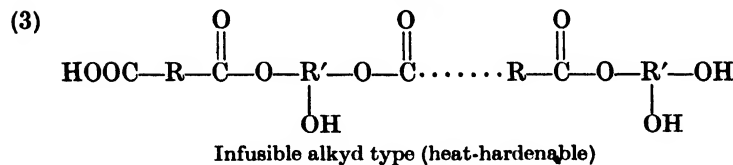
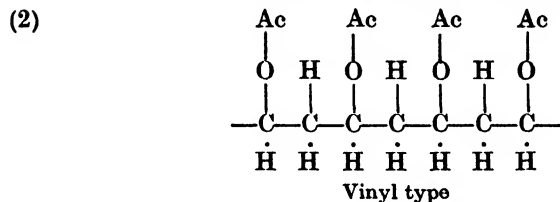
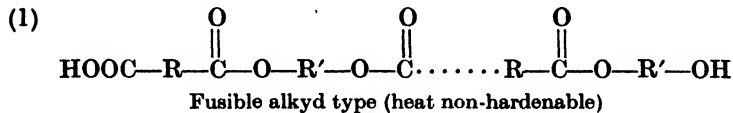
Harvey¹⁰⁸ has described the production of a resin from the non-drying oil obtained from the shell of the cashew nut condensed with formaldehyde. The resin is marketed as 'Harvel' and is very resistant to acids and alkalis and to the softening action of mineral oils. Consequently it has been used for impregnating paper from which screw stoppers for bottles are made, for lining acid-baths, and as flooring material in garages.

S. D. Shinkle, A. E. Brooks, and G. H. Cady¹⁰⁹ describe a new class of plastic material 'AXF', formed when an ethylene dihalide reacts with an aromatic hydrocarbon of the type $R \cdot C_6H_4 \cdot R$, in the presence of aluminium chloride. This plastic is useful as a com-

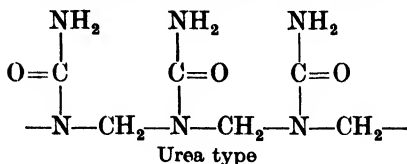
pounding ingredient with natural or synthetic rubber. The breaking elongation, flexibility, resistance to ozone, oil, and gasoline of semi-hard rubber stocks may be increased by addition of 'AXF'.

It has excellent plasticizing action on Duprene and Thiokol, but differs from the latter in being non-vulcanizable (cf. Chapter XIII).

It is now possible to summarize the main types of synthetic resins described in the foregoing pages and to draw some conclusions from the reactions occurring. If the type formulae for the various synthetic resins which have been advanced by Allen²¹ and his co-workers be compared, there is an observable similarity:



(5)



All the foregoing types of structure are chain-like. In class 1 the linkages are ---C---O---C--- , and there are no possibilities for cross linkage. The properties of resins in this class correspond with such a structure: they are fusible solids or viscous liquids.

In class 2 the linkages are ---C---C--- , but without cross linkage, and such resins are truly thermoplastic.

In class 3 the linkage is again ---C---O---C--- but here there is an opportunity for cross linkage. Resins of this type may become infusible and heat-hardenable. They possess some of the properties of those in class 2, because the completely hardened resins may be rendered plastic and apparently depolymerized by mechanical working.

Class 4 exhibits the ---C---C--- linkage with a cross linkage between the chains which also may be ---C---C--- . Such resins may become infusible and are heat-hardenable. In their final infusible state (4a) they are rigid and not subject to depolymerization.

The linkage in class 5 is ---C---N---C--- , and the same group is in the cross linkage and these become infusible and heat-hardenable. It is suggested that the ---C---C--- linkage is probably a stronger bond in some respects than either ---C---N---C--- or ---C---O---C--- linkage, since both type 3 and type 5 are less resistant to water than is type 4. The structure of the chain is reasonably well established, but the exact nature of the cross linkage is somewhat uncertain.

Modifications of the above structural formulae as the result of recent research are given in chapter XVI on the Problems of Resinification.

It must not be assumed that there is any regular arrangement of molecular chains and complexes in the final infusible form of these synthetic resins. Rather must one picture a tangled mass of molecules of structures fashioned along the lines suggested above by Allen, Meharg, Schmidt,²¹ and others (see Chapter on the Problems of Resinification).

The trend of current research is to give great consideration to condensation and polymerization, and in discussing the nature of resins G. T. Morgan¹¹⁰ stresses the powerful influence of cross-linkings in the building up of molecular complexes.

C. Ellis,⁶³ illustrating his views by reference to various synthetic resins, rubber, hydrocarbons, cellulose, &c., discusses polymerization somewhat fully, and distinguishes two general types of manipulation or 'tailoring of the long molecule', as he prefers to call it: (a) polymerization of simple derivatives to give high molecular weight bodies; (b) degradation of the natural macromolecules. He concludes

that studies in polymerization processes will lead to production of newer types of resins, but to attain this end a knowledge of polymerization reactions is essential, so that work may be directed to production of resins having desired properties and capable of meeting new and specific industrial requirements.

A study of such natural products as starch, cellulose, rubber, silk, chitin led H. Mark¹¹¹ to the conclusion that their structural principle is similar to that of synthetic resins. Polymerization and polycondensation reactions lead mostly to the production of macromolecular substances, and macromolecules may be chains or a 2- or 3-dimensional network, and Mark considers that the mechanism by which long chains are built up should be studied systematically.

Actually, the shape, reactivity, mechanical, and optical behaviour of many of these large molecules have been studied. But the whole polymerization process is very complicated, even for the chains, and depends on solvent, temperature, pressure, presence of catalytically active bodies, &c. So far, no polymerization process has been quite resolvable into all its elementary steps.

A useful summary on the same subject has also been made by H. Dostal, H. Mark, and R. Ruff.¹¹²

Quite recently R. V. V. Nichols and P. Larose,⁴⁶ discussing the significance of molecular structure in relation to properties of resins, point out how such properties as thermal behaviour, pliability, and tensile strength are related to the idea of a macromolecular structure.

Properties of the resins are also affected, they say, by the type of 'back-bone' linkage. Thus the —C—C— type imparts water resistance and dielectric strength. Ester linkage, as in the alkyds, and amido-linkage as in polyamides, are susceptible to hydrolysis and are not stable in strong alkalis. Presence of phenyl groups decreases elasticity, while substituent chlorine atoms, as in polyvinyl chloride and polychloroprene, confer extreme chemical resistance.

Types of Synthetic Resins.

The outstanding types of synthetic resins used as moulding materials are:

1. Phenol-formaldehyde resins. These are thermo-setting and are used for moulding powders, for cast plastics, and laminated materials.
2. Furfural resins. These also are thermo-setting and are used for moulding and cold moulding.
3. Urea and thio-urea resins. These are thermo-setting and form the basis of Beetle ware.
4. Glyptals. Some of these are thermo-setting and some thermoplastic. They are used in the manufacture of composite mica articles.
5. Coumarone and indene resins, though not moulding materials, can be incorporated in such materials in certain cases.
6. Vinyl and styrene resins. These are thermoplastic and can be

moulded to clear transparent solids. They vary in consistency from rubbery materials to brittle resins. Some have been used in dentures.

7. Acrolein and urea resins. These are suitable as electrical insulating materials.
8. Sulphonamide resins. Some of these are thermo-setting and may be used for moulded articles. Others are used for insulation work.

The outstanding types of synthetic resins finding application in the varnish and lacquer industries^{21,113} to-day in order of importance are the following:

1. Phenol-formaldehyde condensation products yield spirit-soluble resins for electrical insulation and they can be compounded with nitro-cellulose lacquers. Oil-soluble types are formed also. Others are compounded in clear cellulose lacquers to increase adhesion and durability.
2. Polyhydric-polybasic or glyptal types, both air-drying and baking types. Some are spirit soluble, some soluble and drying oils, and others are modified by incorporation with rosin (colophony) and thus are varnish gum substitutes. Others again are compatible with nitro-cellulose lacquers. Some types find extensive application.
3. Furfural types find use in insulating varnishes and lacquers, and the oil-soluble type is compatible with tung oil.
4. Urea and thio-urea types. A few are used as stoving lacquers and finishes, but seldom alone, while others are compatible with nitro-cellulose.
5. Coumarone and indene types form oil-soluble resins.
6. Vinyl and styrene ester polymers are used in lacquers and in nitro-cellulose finishes.
7. Monocyclic ketone condensation products form oil-soluble resins.
8. Chlorinated diphenyl resins, petroleum hydrocarbon resins also used as varnish resins in restricted fields.

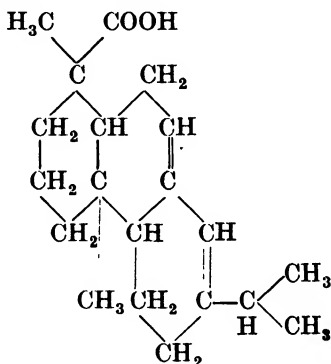
Ester Gums (cf. Chapter VIII).

Untreated rosin (colophony) is too soft, too acidic, and too sticky to be used in varnish making, and the resultant film is neither durable nor waterproof. Moreover, rosin drying-oil varnishes, on exposure, turn white and cloudy owing to emulsification set up by moisture on the components of the varnish film. Attempts to overcome these recognized disadvantages inherent in the use of rosin in oil-varnishes have been successful in two directions by production of (a) hardened rosin, (b) ester gums, in which the acids of rosin are combined with glycerol.

Hardened rosin was first produced by neutralizing rosin with lime and other bases, and its use was greatly enhanced when it was shown that such hardened rosin could be used with advantage in tung oil (China wood oil). The gelation and more uniform setting of this oil

are facilitated by admixture both with hardened rosin and ester gums.

Rosin and glycerol react, though not to complete neutrality, to produce esters. Glyceryl esters of rosin were first introduced into the United States in 1893, but many years elapsed before their use was widely developed.¹¹⁴ These glyceryl esters are simply esters of the natural resin acids and presumably have a similar structure to the latter, being based on that of abietic acid whose structure was shown by Ruzicka^{115, 116} to be as represented in the formula given, i.e. based on phenanthrene. His investigations extended to kauri and copal, the structure of the latter bearing the same relationship to trimethyl-naphthalene.



Many of the copals have high acid values and cause livering in varnishes and enamels containing basic pigments just as do the rosin in oil-varnish films. The preparation of glycerol esters of copals and allied resins has been achieved, though their preparation is not so easy as in the case of the rosin derivatives.

Protein Plastics (cf. Chapter II).

Protein must be hardened to attain its maximum value for industrial application as a plastic, and an aldehyde, preferably formaldehyde, is used for this purpose. Casein plastic is the best known and, so far, the only one to achieve full commercial success, but plastic material from soya-bean protein is now receiving full attention. No success has been achieved up to the present in combining casein with phenolic or other resinous moulding material, though some success has been attained in so treating soya-bean protein.

Actually S. Satow¹¹⁷ worked on proteins in U.S.A. as far back as 1917 when he treated the protein from oil-free soya-meal, after kneading and drying, with formaldehyde and obtained a completely thermoplastic material. Complexes of the phenol-formaldehyde-amine type have been exploited by Henry Ford, who has used the protein group in soya-meal to make the so-called soya-bean plastic for use in the automobile industry.¹¹⁸

A. C. Beckel, G. H. Brother, H. Chase, and L. L. McKinney¹¹¹ have examined the properties of protein plastic from soya-bean products, and have found that soya-bean protein has properties different fundamentally from those of casein. Soya-protein has the property of plastic flow even when the moisture content is reduced to that approximating to chemically bound water.

Addition of water to soya-protein or -meal leads to a product similar to casein-plastic, whereas reduction of water below 5 per cent. gives a *zein*-like plastic.

Developments may be expected when more is known of the protein structure, and W. T. Astbury¹²⁰ has made this matter the subject of some study.

G. H. Brother and L. L. McKinney¹²¹ in some further work on the subject believe that a practical moulding material might be made out of the thermoplastic material derived from soya-bean protein, if a suitable plasticizer could be found.

Casein plastic material, marketed in England under the name 'Erinoid', is a by-product of the milk industry, being prepared from casein which is contained in colloidal suspension in cow's milk. This plastic material is made here by Erinoid Limited, a related product, 'Lactoid', being made by British Xylonite Limited, and under the name 'Galalith' it is made both in Germany and in England. After removal of the cream, the separated milk contains about 3 per cent. of its weight of casein which is a phospho-protein, being composed of a lime compound of protein in combination with calcium phosphate. The protein character is an indication that the molecular structure is complicated. Casein has, of course, been known from time immemorial as the curds in the milk of all mammals, but its industrial use is comparatively recent.

More knowledge of the structure of the casein molecule is desired, and till this is forthcoming the industry is likely to remain under some handicap.

In the glazing of paper, in waterproofing, as an adhesive paint and cement, and in the manufacture of cold-water paints and distempers, and in other preparations where its adhesive properties proved valuable, casein came into use many years ago. Some account of its uses and properties and the technique of its manufacture have been described by C. H. Butcher.¹²²

Krische, experimenting in Hanover about 1897, found he could produce films from casein solutions and that these films could be hardened and rendered waterproof by chemical treatment. Later, Spitteler in Bavaria, together with Krische, discovered the reaction whereby casein could be hardened by formaldehyde. Following an English patent in 1897 and the work of the Russian, Schutze, a process was devised for the production of a tough, horn-like, plastic material. Ultimately the cycle of operations was brought to technical perfection and commercial success achieved in this country by a process which has been described by R. Dodd.¹²³

The first stage in this process comprises the preparation of the

casein in comparatively pure condition by means of the rennet ferment: this gives the best type of coagulation and results in a tougher casein plastic. What is known as the 'dry process' is now favoured. The ground casein, mixed with fillers and pigments, is subjected to heat and pressure in extruding machines where the plasticizing occurs. The material leaves the extruding machines in the form of rods and tubes of soft, rubbery consistency. Hydraulic presses convert the rod and tube form of the plastic into sheets, which rapidly harden. Final subjection to formaldehyde in treatment tanks, lasting from 10 days to 10 weeks according to conditions and requirements, completes the operation.

Quite recently R. W. Smith¹²⁴ described a continuous method of casein manufacture in contrast to the older established batch process. In the new process the precipitation of the casein is effected at the correct acidity, an acid method of coagulation thus replacing the rennet method. The acid is separated from the whey in an inclined trough, and the solids are removed by a screw conveyer and carried to a press. On leaving the press the casein contains 50 per cent. water, hot air removing the rest, after which the dried casein is ready for use. It comes on the market as a white or yellowish, crumbly powder, which after suitable grinding is ready for use as a plastic material in the manner described in the above paragraph.

The finished material is fabricated like horn and ivory, and as a decorative material is of great value. At 130° it begins to discolour and at about 200° is completely disintegrated, but at no time is it inflammable.

Casein plastic is hygroscopic, and as the material can be softened and moulded in hot water this is of considerable advantage. Although an excellent insulator, it cannot be employed for high-tension work and on account of its hygroscopic character is useless on all outdoor work.

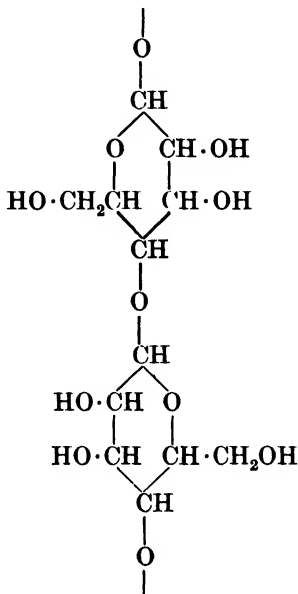
Discussing recent developments in casein plastic G. H. Brother¹²⁵ mentions that in U.S.A. it was known first as 'Aladdinite', then as 'Karolith', 'Kylloid', 'Inda', and finally 'Erinoid'. Different climatic conditions in U.S.A. have restricted the use of casein plastics there to buttons, buckles, and other small objects. Two lines of improvement have been followed: (a) shortening of the hardening time; (b) substitution of a dormant hardening agent for formaldehyde.

Cellulose Esters and Ethers (cf. Chapter II).

Cellulose is the fundamental chemical compound in all vegetable matter, the fibres of which are built up of a chain of molecular units of empirical composition expressed by the formula $(C_6H_{10}O_5)_n$. The interlocking of these chains partly accounts for the high tensile strength of the fibres. Its abundance, cheapness, and freedom from colour make cellulose valuable as a basis for plastic and allied materials, but its sensitiveness to atmospheric changes is its great drawback. It does not soften under heat or pressure, and though solvents are known which will dissolve it, all attempts to regenerate

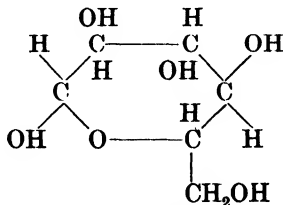
the cellulose from the solutions in masses which can be moulded or in other utilizable form have proved valueless.

The empirical formula $C_6H_{10}O_5$ for cellulose may be put in the form $C_6H_7O_2(OH)_3$, and on the reactivity of the three (OH) groups depends the uses to which cellulose is put in industry.



(Part of the cellulose chain.)

In combination with such acids as nitric or acetic cellulose yields esters known respectively as nitrocellulose and cellulose acetate—actually the trinitrates and the triacetate.



(Glucose)

These have formed the basis of important plastic materials, invaluable under appropriate conditions for moulding; as coatings in the varnish and lacquer industries; as artificial silk, non-inflammable films, transparent paper, &c.

Cotton-seed linters, the seed hair of the cotton plant, represent cellulose in its purest natural form. In wood tissue the cellulose is

associated with other chemical groups, requiring removal before a form of cellulose can be obtained which will give cellulose esters identical with those from cotton. But this is now regularly achieved on a commercial scale, selected spruce pulp being treated by the viscose process.

The cellulose plastic and rayon industries have hitherto depended on cotton linters or wood pulp, mainly derived from America and the Scandinavian countries. V. E. Yarsley,¹²⁶ commenting on this, draws attention to the work done on the Continent and to the consideration given to the use of hemp straw and fibre. Success has been achieved in Italy and South America in the production of high-grade bleached pulp straw for rayon and paper. A little modification might convert this to cellulosic plastic material.

G. J. Esselen¹²⁷ classified cellulose and its derivatives under the following convenient headings:

- (a) Cellulose used as such, including: paper, three types of rayon, transparent wrapping 'Cellophane'.
- (b) Cellulose nitrate as the ultimate form: pyroxylin plastic (celluloid), photographic film, cements, lacquers.
- (c) Cellulose acetate as the ultimate form: cellulose acetate type of synthetic fibres, transparent wrapping material (Kodapak), photographic film (non-inflammable), new slow-burning plastic material to replace celluloid.

Only materials coming within the second and third headings will be discussed here.

Nitrocellulose. A large number of nitrocelluloses are known, the highest nitrated forms being used as a basis of gun-cotton. Low nitrated cellulose containing about 10.5 to 11.1 per cent. nitrogen forms the basis of celluloid and the nitrocellulose lacquers and finishes. Cotton linters, dried to a uniform moisture content of 1 per cent., are nitrated in the presence of sulphuric acid, the operation being most important as the conditions of nitration as regards time, temperature, and concentration largely determine the constitution and properties of the resulting nitro-cotton. Dehydration to remove water, followed by kneading with camphor, natural or synthetic, in the presence of alcohol until a stiff dough is obtained are the next operations in celluloid manufacture. Celluloid is the pioneer substance in this group, having been patented in 1865 by Alexander Parkes,¹²⁸ who showed the strong solvent power of camphor, dissolved in alcohol or turpentine, for nitrocellulose. Other trade names were Pyralin, Viscoloid, Fiberoid. The word Celluloid is a registered trade name in the United States, where the early industrial development was undertaken by the brothers Hyatt at their printing works under the name of the Celluloid Manufacturing Company. Xylonite was the name adopted for the new material in Great Britain, though the early industrial development here was not successful until 1877, due then to the British Xylonite Company. Addition of colouring matter to the plastic celluloid dough precedes its calendering, after which it is

sliced into sheets, polished, and converted into rods and tubes for use in manufacturing operations. All the materials used in this series of operations—nitric and sulphuric acids, alcohol and camphor—are abundant and relatively cheap. The same may be said of the solvents with which nitrocellulose is incorporated when making nitrocellulose lacquers. The popularity of the latter depends on the rapidity with which they dry, leaving a hard surface resistant to moisture.

Flexible photographic films in which celluloid was used were first manufactured in 1884 by Eastman, and this development now constitutes an enormous industry based on nitrocellulose and cellulose acetate films.

The world production of celluloid is about 40,000 tons per annum.¹²⁶

Cellulose acetate. The inflammability of nitrocellulose and celluloid is a serious drawback to their use, and attempts were soon made to use cellulose acetate which is not inflammable though it will burn slowly. In this development serious difficulties were soon met: Schützenberger¹²⁹ carried out the first acetylation under pressure, but this method made no headway. The foundation of the present-day manufacture was laid by Franchimont,¹³⁰ who used sulphuric acid as the condensing agent for cellulose and acetic anhydride. Cross and Bevan¹³¹ took out the first British patent in 1894, but the acetylation was slow and the only solvents that could be used were both costly and toxic, and the resultant acetate was not very stable and became brittle on keeping. G. W. Miles¹³² showed that this primary product could be converted to a secondary acetylated product by partial hydrolysis, this being a most important development. The Dreyfus patents stressed the importance of limiting the amount of moisture in cellulose and the amount of condensing agent used.

Briefly, the reaction between cellulose, acetic acid, and acetic anhydride in the presence of sulphuric acid as the condensing agent leads to the formation of cellulose acetate in solution. After chemical treatment to modify the solubility, cellulose acetate is precipitated, washed, dried, and ground. Its conversion into plastic material is effected by kneading with such solvents as acetone and alcohol and with plasticizers and softeners, such as dimethyl-phthalate, diethyl-phthalate, glycol-phthalate, triphenyl- and tricresyl-phosphates, triacetin and amyl tartrate among the commoner ones. The addition of dye solution or pigment is made to the cellulose acetate dough, after which rolling, pressing into blocks, slicing into sheets, &c., take place. The dough may be extruded in the form of rods or tubes, or converted into moulding powder. The latter flows under heat and pressure and can be moulded in plain or figured moulds.

The growing production of cellulosic plastics in the United States is accounted for by the increased output of cellulose acetate in connexion with the manufacture of laminated glass, but more particularly to meet the demands for injection moulding.¹²⁶

GENERAL INTRODUCTION

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The most important industrial application of cellulose acetate is in the production of artificial silk, but the acetate is being increasingly used to make films, e.g. transparent wrapping films for covering food-stuffs, for non-inflammable photographic films, and in electrical insulation work. In all these developments the non-inflammability of cellulose acetate films is of supreme importance.

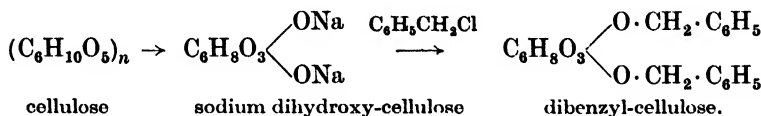
In the decorative coating industries a large range of suitable solvents now available for cellulose acetate make it possible to get this into solution suitable for spraying. Yet despite these developments in the use of cellulose acetate lacquers, nitrocellulose lacquers still retain their superiority over the former as decorative coatings. The catalytic production of cheap acetone, acetic acid, and acetic anhydride have greatly aided the commercialization of cellulose acetate. The wide range of relatively cheap new organic solvents and plasticizers made available in the past few years have made possible many of the developments based on cellulose acetate.

Cellulose ethers. As the (HO) groups of the cellulose molecule react with acids to form cellulose esters, such as described in the foregoing pages, so also do they react with alcohols to form ethers. The first of these to find industrial use was methyl-cellulose, protected by the F. Bayer Company in 1912,¹³³ but benzyl- and ethyl-cellulose soon followed and found greater use. Wood cellulose is converted by caustic soda to soda cellulose which in turn, by heating with benzyl chloride, becomes dibenzyl-cellulose. This is thoroughly purified by washing with water. Ethyl-cellulose is made by a similar process, ethyl chloride being used. Both the benzyl and the ethyl derivatives are converted into plastic material in the same sort of way as that employed in the case of cellulose acetate plastic. By reason of their stable properties, cellulose ethers are used in the manufacture of safety glass as they do not discolour in sunlight. These cellulose ethers can be worked up into lacquers and finishes by utilizing linnoxyn as the plasticizing material.

Ethyl-cellulose is made by the Hercules Powder Co. Inc., Wilmington, Delaware, and W. Koch¹³⁴ has shown that a definite relationship exists between the number of ethoxy groups or degree of ethylation, and the solubility of ethyl-cellulose in both single and mixed solvents. Substitution has a marked effect on the softening-point and in the range 40-49 per cent. ethoxyl. Ethyl-cellulose is quite thermoplastic.

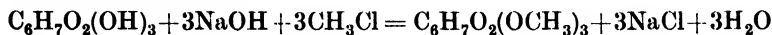
Used in inks, ethyl-cellulose produces 'short' flexible, glossy inks of high quality that do not embrittle with age.

Probably the reactions which occur can be represented as follows:

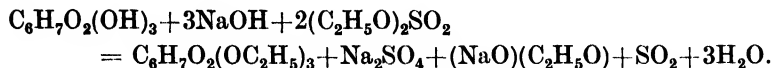


Clément and Rivière¹³⁵ suggest the following equations as represent-

ing the course of the reactions, in which an alkyl halide or alkyl sulphate is employed:



or



Generally speaking, the product is a mixture of mono-, di-, and tri-alkyl celluloses.

Hard Rubber (cf. Chapter XII).

This is better known by its early trade names—ebonite and vulcanite, pioneers of the plastics industry. In broad view, hard rubber is produced by continuing the vulcanizing process of raw rubber beyond the stage at which ordinary soft rubber is obtained. Whereas ordinary soft resilient rubber contains 3–5 per cent. of sulphur, hard rubber contains 20–30 per cent.

The source of rubber is the exudation from the tropical forest tree, *Hevea brasiliensis*, indigenous to the Amazon forests, but now cultivated in plantations in Ceylon, Indo-China, British Malaya, and the Dutch East Indies. This exudation, the hevea latex, contains about 35 per cent. of rubber in colloidal suspension in water. The dried coagulum is raw rubber, an unsaturated hydrocarbon of the empirical formula $(\text{C}_5\text{H}_8)_n$. Raw rubber is tacky on heating, stiffens with cold, and perishes with age. Present-day industrial application of rubber is due to Hancock, who found in 1820 that, by rolling, a plastic mass was obtained which could be moulded.

Vulcanization, or the heating of rubber with sulphur mixtures, became a recognized process after the work of Charles Goodyear in the United States in 1839, and Thomas Hancock in Great Britain in 1842. Their early efforts were consolidated in Germany by O. Mayer in 1854 and the foundation laid of the use of vulcanized rubber as a moulding material.

The plastic mixture of raw rubber and sulphur softens with the first application of heat and can then be pressed into sheets, formed into rods and tubes, or shaped in moulds by hydraulic pressure. Mineral powders such as carbon black, zinc oxide, colloidal clay may be added to alter the mechanical properties of hard rubber or to raise the temperature at which it softens. Its flexibility may be modified by incorporating oils and waxes, while its decorative value can be greatly enhanced by incorporating suitable pigments. Thus a wide range of colour, density, elasticity, and resilience, specific electrical resistance and resistance to abrasion can be secured by suitable additions. Anti-oxidants prolong its life and accelerators speed up the rate of vulcanization. It can be made resistant to corrosive chemicals and impermeable to liquids.

Vulcanite is not so resistant to abrasion as ordinary soft rubber

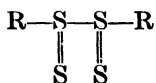
though more resistant to chemicals. From the foregoing paragraph it is clear that a wide range of hard rubbers can be made, varying in properties and spheres of usefulness in accordance with the amount of sulphur and other ingredients and the degree of heating applied. Hard rubber is non-poisonous, non-absorbent, and without odour, chemically inert, though prolonged immersion in the usual rubber solvents causes it to soften and swell.

Its mechanical properties have made it a valuable material, as its tensile strength is 1,000 to 10,000 lb. per sq. in. and its compression strength 3,000 to 20,000 lb. per sq. in. Though it can be used up to a temperature of 150° F. the fact that it softens at comparatively low temperatures is a serious drawback to its usefulness.

The electrical properties of hard rubber are remarkable: the dielectric strength is 25,000 to 40,000 volts per mm., and in electrical insulation work this material has in the past found its main outlet. In high-frequency work, where low electric energy absorption is so important, hard rubber is still without a rival. While their non-hygroscopicity and impermeability to moisture are outstanding advantages, the failure under heat and the marked lowering of insulation resistance of the ordinary black electrical grades under exposure to light, are the chief drawbacks of these hard rubbers.¹³⁶

Polysulphide Rubbers (cf. Chapters XIII and XVI). S. M. Martin, jr., and J. C. Patrick¹³⁷ have described the formation of many high molecular weight polysulphides by reaction between organic dihalides with terminal $-\text{CH}_2\text{Cl}$ and inorganic polysulphides. These resultant compounds have rubber-like properties and are of great use in articles requiring flexibility and elasticity at temperatures as low as -40°C . (-40°F .), coupled with the power of resistance to solvents such as petrol and oil. Hence they can find use in rubber printing plates and for the manufacture of gasoline paint spray hose.

These compounds are thought to be long-chain polymers in which the organic radicals are converted through $\text{R}-\text{S}-\text{S}-\text{R}$ linkages and the added sulphur is probably linked thus:



Buna Rubbers (cf. Chapter XII). Recent work on the structure of polymeric materials has given knowledge leading to the production of many synthetic compounds of high molecular weight. Some such are notable for their rubber-like, elastic properties.

A. Koch¹³⁸ has described some of these products as made by the I.G. and known in Germany as Buna Rubbers, where they are made in large quantities. They have poor mastication properties and inferior tackiness, but it is claimed for them that they are superior in heat resistance and abrasion resistance when compared with natural rubber.

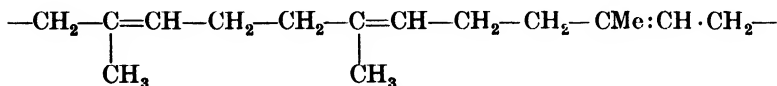
Buna 85 is a pure butadiene polymer, Buna S a mixed polymer of butadiene and styrene, and Perbunan a mixed polymer of butadiene and acrylic nitrile. Highly polymeric butadiene rubber is very hard and so is difficult to compound. Plasticization, processing, and vulcanization are as with natural rubber.

Chlorinated Rubber (cf. Chapter XII).

Produced by the action of chlorine on unvulcanized rubber, this is an allied material of growing importance. Many attempts have been made to transform natural rubber into derivatives similar in properties to those of nitrocellulose and other varnish-making materials. The original patent on chlorinated rubber was filed by Peachey in 1916, although A. V. Newton in 1859 brought out a patent referring to the action of gaseous chlorine on rubber.

As a white powder under the name 'Alloprene' and with a chlorine content of 65-67 per cent., and of approximate empirical formula $C_{10}H_{13}Cl_7$, chlorinated rubber is now being marketed on account of its valuable film-forming properties. Soluble in a wide range of industrial solvents, miscible with many common plasticizers, it can be formed into films comparable with those formed from cellulose acetate and nitro-cellulose. Non-inflammable, insoluble in water, unattacked by strong acids and alkalis, it is valuable as a coating material for iron pipes and concrete.¹³⁹

Hard rubber and chlorinated rubber may be related to the vinyl and styrene resins, with which they have in common the property of chemical inertness, and though chlorinated rubber is not yet produced in a form suitable for moulding purposes, hard rubber and the vinyl and styrene resins are moulding materials. Rubber is probably a linear chain of units of the conjugated isoprene molecule



This contains the vinyl group ---CH=CH_2 already noted in styrene and vinyl compounds. It is not unlikely that a structural relationship may exist between styrene and vinyl resins on the one hand, and hardened and chlorinated rubbers on the other.

H. R. Thies and A. M. Clifford¹⁴⁰ describe a moulding resin, Plioform, formed by the reaction of rubber with chloro-stannic acid. These recently developed rubber derivatives are odourless, tasteless, and resistant to all alkalis and most acids. They are thermoplastic and form a tough non-shatterable resin, which appears to offer a wide field as a plastic material and a substitute for hard rubber. These resins are also described by Chase.¹⁴¹

Plioform, produced by sheeting plioform, is now available in a great variety of colours and its properties make it of great value as a wrapping for many foods, cosmetics, &c., where retention of

flavour or odour is desirable, as well as providing protection from moisture.

A. Jones¹⁴² has described many of these chlorinated rubbers, sold under such names as Tornesit, Tegofan, Pergut, and their use as anti-corrosion paints in chemical factories. These rubbers are odourless, able to withstand hard wear, do not begin to decompose before 150°, are completely incombustible, and do not fire on exposure to flame. They are not affected by steam, corrosive fumes, acids, alkalis, salts of the most varied kind, fatty acids, glycerine, and most organic solvents, lubricating oils, and paraffin wax. In general they have a fire-extinguishing effect.

J. P. Baxter and J. G. Moore¹⁴³ have also summarized similarly the properties and uses of chlorinated rubber.

Some Recent Applications of Plastics.

Plastics find applications in medicine and surgery (*Plastics*, 1941, 5, 12) such as the use of phenolic mouldings for X-ray machines; cellulose acetate sheet for surgical masks; the production of surgical and dental instruments from glass-clear acrylic resins; surgeon's thread from nylon; polyvinyl resin extruded tubes in place of rubber ones for drawing off body fluids.

In addition to the well-known vulcanite dental plates are 'Oralite', a nitrocellulose plastic prepared for denture purposes, and the use of solid polymerization products of polystyrol, polyvinyl or polyacryl compounds represents another development in the application of plastics to dental work. Typical of the latter is the use of styrene in admixture with powdered polymerized methyl methacrylate aided by a suitable accelerator (B.P. 498, 877).

H. S. Taylor (*Nature*, 1940, 146, 768) discussing the kinetics of contact catalysis in relation to some recent industrial developments in the use of plastics, points out that progress in some of the newer researches arises from the discovery that 'cross polymerization', the introduction of other molecules into the growing unit, shows rubber, the plastics, cellulose, starch, &c. to be macromolecular, i.e. composed of large numbers of constituent units combined with each other into a structural pattern each conferring on the mass its particular characteristics.

The newer synthetic rubbers build into the growing butadiene polymer such other substances as styrene and acrylic nitrile, resulting in products having abrasion characteristics and resistance to oxidation, making them better in these respects than the best natural rubbers. 'Neo-rene' and 'thiokol', containing chlorine and sulphur respectively, in addition to their carbon and hydrogen constituents, deviate markedly in constitution from the natural product and possess unique properties making them for certain purposes more valuable than the natural product.

Out of some of these researches have arisen the newer synthetic fibres of which 'nylon', now in large-scale production, is in many ways superior to silk.

STATISTICS

Statistics for the Production of Synthetic Resins.

The growth of the synthetic resins and plastics industry has been phenomenal. Statistics for the production of synthetic resins in this country are not available, but it is believed that the annual increase is about 15 per cent. Only in the sphere of the phenolic resins can figures from 1910 be given.

H. V. Potter¹⁴⁴ states that in 1910 a few workers were engaged on phenolics, and by 1914 the number had grown to about 100. At the end of 1934 it was estimated that 1,500 persons were working directly on resinoid manufacture, and 10,000 in moulding and laminated processes, representing a total capital of £2,500,000. In 1937 £2,000,000 were invested in the manufacture of plastic materials; £5,000,000 in the fabricating side of the industry; 25,000 workers with a turnover of £7,500,000 per annum, cf. 75,000 in the chemical industry with a turnover of £67,324,000 per annum. The output efficiency per worker was £900 per annum in the chemical industry; £850 per annum on the plastics raw material side and £300 per annum on the plastics fabricating side. The national requirements are: 1.09 lb. plastics per head of population in Great Britain; 1.49 lb. plastics per head of population in U.S.A.; 1.5 lb. plastics per head of population in Germany. These figures do not include plastics from casein, cellulose, bitumen, and shellac, or tool or mould-makers. According to a report of the U.S.A. Tariff Commission for 1934-8¹⁴⁵ the production of coal-tar resins increased from an average of 12,221 short tons in 1925-30 to 20,814 in 1933, and 28,854 in 1934 (1 short ton = 2,000 lb.), and 53,000 short tons in 1938. The 1934 production included resins derived from phenol or cresol 20,327, from phthalic anhydride 7,438, and from styrene and xylene 88 short tons. The figures for the styrene resins are interesting and, although only made on a small scale, it is evident that there is a demand for these clear, colourless products with their good dielectric properties. Germany¹⁴⁶ manufactured about 16,000 tons of plastic materials in 1934, of a value of about 23 million marks, about one-third of the production being exported. Plastics are making headway in Australia, where a firm is manufacturing phenolic moulding powders. Russia is reported to be building new plants for the production of formaldehyde from methyl alcohol and from natural gases.

The production of urea resins in the U.S.A. increased from 2,250 short tons in 1934 to 3,109 short tons in 1935, and to 4,500 short tons in 1938, and the vinylite type from 500 short tons to 2,000 short tons in the same period.

In the U.S.A. cellulose acetate plastics have increased from 100 short tons in 1931 to 5,500 short tons in 1935, and to 7,000 short tons in 1938. The nitrocellulose plastics show a decrease in production due, no doubt, to the lowering of the price of acetate plastics from 1931, but an increase from 6,180 short tons in 1934 to 8,102 short tons in 1935, followed by a decrease to 4,250 short tons in

1938. In 1938 the production of synthetic resins other than coal-tar resins had risen to 10,500 tons.

The following table shows the production and sales of synthetic resins in 1937 in the U.S.A. in more detail:

Synthetic Resins in the U.S.A. in 1937 [Br. Plastics, 1938, 10, 228]

	<i>Short tons</i>	
Resins from cresols or cresylic acid	Production	5,350
	Sales	4,233
Phenol resins	Production	26,236
	Sales	25,105
Phenol/cresol resins	Production	7,023
	Sales	6,620
Xylenol resins	Production	320
	Sales	321
Xylenol/cresol resins	Production	993
	Sales	499
Alkyd resins (from phthalic anhydride)	Production	29,225
	Sales	16,300
Alkyd resins (from maleic anhydride)	Production	1,400
	Sales	1,177
Resins of non-coal-tar origin (including polyvinyl, acrylic acid and amino-plastics resins)	Production	10,500
	Sales	9,450
	Total production	81,047
	„ sales	63,705

L. A. Jordan (*Chem. and Ind.*, 1937, 56, 484) estimates the U.S.A. consumption for resins in the paint and varnish industry to be:

	<i>Metric tons</i>
(a) Reduced phenolic resins	15,000
(b) Pure phenolic resins	3,000
(in comparison with phenolic resins for moulding powders)	
	10,000
(c) Alkyd resins	12,000

In turn, the British consumption of these products as far as items (a), (b), and (c) are concerned is about one-tenth of the above figures.

In 1938 the output of thermo-setting resins in Great Britain was estimated at 20,000 tons per annum and in U.S.A. at about the same figure.

In 1931 the world production of cellulose acetate was 1½ per cent. that of celluloid, and it has increased to 74 per cent. in 1937 (Jan.-Sept.). The world production of celluloid in 1937 was 40,000 tons, of which Great Britain used 3,000 tons.

There are no available figures for comparison in this country, but it is estimated that, deducting the products not made in this country, the production of the British Plastics industry will compare very favourably with that of America not only as regards total, but also in respect of the very large increases that have taken place in the various materials.¹⁴⁷

At the present time it is suggested by Megson and Pepper¹³ that

the world production of synthetic resins, excluding cellulose and casein plastics, is at the rate of 150,000 tons per annum. Of this total Great Britain is said to produce 30,000 tons.

H. Levinstein (*Chem. and Ind.*, 1939, 58, 189) stresses the need for national planning in connexion with the import of plastic materials. He divides plastics into three groups:

Group 1. Those which can be made in Great Britain from its own raw materials, e.g.:

- (a) Phenolic plastics; phenol formaldehyde moulding powders; the world's production is 100,000 tons annually, of which Germany provides 30,000 tons.
- (b) Amino-plastics.
- (c) Cellulose (acetate and nitrate). The U.S.A. in 1933 produced nearly 13 million lb. celluloid and nearly 3 million lb. cellulose acetate. In 1937 the output was 18 million lb. celluloid and nearly 19 million lb. cellulose acetate (Bureau of Census (U.S.A.)).
- (d) Glyptals.
- (e) Polystyrenes (distrene).
- (f) Methylmethacrylate polymers (Perspex).

Group 2. Those made in Great Britain from imported materials:

- (a) Casein plastics.
- (b) Vinyl plastics (Mipolam).
- (c) Bitumen plastics, e.g. from gilsonite.

Group 3. Those not made in Great Britain:

- (a) Gelvas and alvars.
- (b) Polysulphide plastics.
- (c) Ketone condensation resins.
- (d) Buna (60,000 tons production in 1938; the Russian type 20,000 tons, and *neoprene* of the Du Pont Co.

CONCLUSIONS

During the past few years an enormous number of patents and papers have appeared dealing with the synthetic resin industry. While very many of these are of no importance, it is possible to discern certain definite lines along which progress is being made and which hold out the promise of further development in an industry which is still in its infancy.

F. Sproston,¹⁴⁸ reviewing the rise of the plastics industry, tabulates its fifty years' progress from the first of the modern plastics to be discovered, the nitrocellulose-camphor plastic, and correlates this with advances in organic chemistry. Sir G. T. Morgan,¹¹⁰ discussing the trend of research, mentions the growing importance of chlorinated rubbers, the development of transparent materials, especially the vinyl and methacrylate types, and their industrial importance: that the latter field holds out considerable promise for the future is borne out by a review, which shows the demands now made on the

transparent plastics industry by the claims of transport and national defence requirements, and by the needs of the food industries for wrapping and packaging materials.

There is an increasing tendency to make use of resins in the form of emulsions. H. W. Hutton¹⁴⁹ forms phenol formaldehyde-type resins in the presence of a stabilizer, and a saponifiable substance such as a sulphonated oil as emulsifier, water as the dispersion medium being added afterwards. Addition of suitable binders followed by de-watering, drying, and calendering as in the paper industry results in sheeted material, which can be moulded to give electrical parts of superior insulating and mechanical properties.

Bakelite Limited^{150, 151} are responsible for two patents relating to improvements in the production of such resin emulsions to be used for coatings, and more recently the I.G.¹⁵² have patented the condensation of carbonyl compounds with hydrolysed polyvinyl esters while the latter is dispersed in water. Right choice of emulsifier is of supreme importance in these developments(cf. Chapter XIII).

Another development of promise is that which involves the use of cast and moulded transparent phenolic resins of which D. K. Bancroft¹⁵³ and D. Masson¹⁵⁴ have given a good account.

Enormous strides are taking place in the use of injection moulding, particularly the vinyl and acrylate resins, and in cellulose acetate. Resinoid, previously plasticized by heat, is forced through an orifice into a closed mould, thus replacing the use of the resinoid in powder form. Thermoplastics and thermo-setting resins may be used although careful control of temperature is necessary in the process when thermo-setting resins are treated. Some improvements in this type of moulding are due to Thermo-Plastic Inc.¹⁵⁵ and the Celluloid Corporation¹⁵⁶ respectively.

By the addition of suitable fillers, or by use in laminated form by impregnating paper, fabric, and boards, followed by heating and pressure, the phenolic resins have become of great importance as constructional and engineering material. H. V. Potter,^{157, 158} H. V. Potter and A. Lowe,¹⁵⁹ A. J. Weith,¹⁶⁰ and others have described recent progress and possibilities of laminated plastics which may be briefly summarized thus:

- (a) In the building trades as veneers and panels for interior decoration in ships, railways, buildings, &c., and on certain types of furniture. These laminated plastic panels do not stain or corrode, are not affected by water, are hygienic and non-hygroscopic, and so easily keep clean.
- (b) In mechanical engineering for silent and corrosion-resisting gears, roller mill bearings, various automobile parts, both stressed and unstressed.
- (c) In the automobile and aircraft industry. Approximately thirty components of an automobile are now produced in plastics of different kinds. Moulded air-screw blades are also produced.

- (d) In electrical engineering, where the applications are very numerous, plastics have replaced many of the older insulators such as mica, rubber, slate, fibre, porcelain.
- (e) In chemical engineering. Here materials based on phenolic resinoids have the useful property of resisting corrosion as well as resisting shock. These properties are not possessed in all cases by metals, glass, stoneware, rubber, wood, and ceramics (cf. Chapter III).
- (f) In food processing. Structural materials based on tasteless, odourless, non-corrosive phenol-formaldehyde-type resins are finding increasing use in the food-processing and canning industries.¹⁶¹

The application of synthetic resins to the textile industry has stimulated attempts to emulate or improve on proteins, cellulose, and rubber, notably with the object of producing synthetic fibres. Nichols and Larose⁴⁶ have described 'Vinyon', a polymer of vinyl acetate and vinyl chloride, which after undergoing a number of operations peculiar to textiles, yields a uniformly soft filament of high shrinkage value useful in making felts.

Another class of synthetic fibres, the 'Nylons', is made from dibasic acids and diamines, and by the wet process of spinning gives a crenulated fibre good for staple (Exfon), while smooth filaments can be obtained by extrusion of the molten mass (Nylon). W. H. Carothers and Du Pont¹⁶² describe the latent developments in 'Nylon' which is fungi- and bacteria-proof, non-inflammable, can be crimped and set to produce a wool substitute (cf. Chapters XIII and XVI).

H. Levinstein,¹⁶³ discussing the impact of plastics on industry, tabulates the main applications in which they find use. It is a reasonable conclusion, in the present writer's view, that as other raw materials are found suitable and more becomes known of what is the desirable chemical structure of synthetic resins, further manufacturing developments may be expected to bring in their wake further applications of such resins in industry.

Touching this question of what may be a desirable chemical structure of synthetic resins, the following from a report by H. W. Melville¹⁶⁴ is of importance: 'Plastics owe their characteristics mainly to the fact that the constituent molecules are of high molecular weight. The shape of the molecules also plays a very significant part in modifying mechanical and electrical properties.' To make progress, therefore, the size and structure of molecules must be known with certainty and be capable of alteration in a predetermined manner.

Reference must be made to synthetic rubber resins which are described in outline in Chapter XII. For details the reader must consult W. Naunton's book. The furfural, the sulphonamide, and chlorinated rubber resins, although in less demand than the main industry products, possess special properties which require further

investigation on works scale to bring them into technical consideration. In the chapter on the Problems of Resinification a decided advance in the correlation of structure and physical and technical properties has been made during the last few years, especially in the mechanisms of polymerization. A clearer understanding of the functions of secondary valencies and the part played by them in resin formation is much desired.

BIBLIOGRAPHY

- T. H. Barry, *Natural Varnish Resins*, Ernest Benn Limited, London, 1933.
 Herbert Abraham, *Asphalts and Allied Substances*, 3rd Edn., D. van Nostrand Co., New York, 1929.
 Clifford Richardson, *The Modern Asphalt Pavement*, New York, 1908.
 H. M. Langton, *Blacks and Pitches*, Ernest Benn Limited, London, 1925.
 Glues and Gelatines, *Ind. Chemist*, 1925, **1**, 306.
 Robert E. Burk and others, *Polymerization*, Rheinhold Pub. Corp., New York, 1937.
 Carleton Ellis, *The Chemistry of Synthetic Resins*, 1935, 2 vols.

REFERENCES

1. *Ber.*, 1872, **5**, 25, 280, 1004.
2. *Ann.*, 1891, **263**, 283.
3. B.P. 16,247 (1899); U.S.P. 643,012 (1900).
4. U.S.P. 735,278 (1903); G.P. 140,552 (1902)
5. B.P. 12,880 (1902).
6. B.P. 8,875 (1905).
7. *Ind. Eng. Chem.*, 1909, **1**, 149.
8. *J. Roy. Soc. Arts*, 1937, **85**, 243.
9. B.P. 15,875 (1914); G.P. 281,939 (1913).
10. *Ind. Eng. Chem.*, 1910, **2**, 478.
11. *Brit. Plastics*, 1937, **9**, 60 et seq.
12. *Ind. Eng. Chem.*, 1938, **30**, 125.
13. *Chem. and Ind.*, 1940, **59**, 247.
14. *Ind. Eng. Chem.*, 1940, **32**, 293.
15. *Ibid.* 309.
16. *J.S.C.I., Trans.*, 1938, **57**, 169.
17. *Chem. and Ind.*, 1939, **58**, 800.
18. *Ind. Eng. Chem.*, 1934, **26**, 37.
19. *Ibid.*, 1930, **22**, 590.
20. *Chem. and Ind.*, 1936, **55**, 319.
21. *Ind. Eng. Chem.*, 1934, **26**, 663.
22. *Ibid.*, 1913, **5**, 506.
23. *Z. anorg. Chem.*, 1912, **25**, 1945.
24. *Chem.-Ztg.*, 1929, **53**, 493.
25. *Ber.*, 1912, **45**, 206.
26. *J.S.C.I.*, 1930, **49**, 251.
27. *Ibid.*, 1933, **52**, 418.
28. *Z. angew. Chem.*, 1933, **46**, 251.
29. *Ibid.*, 1930, **43**, 1129; B., 1931, 212.
30. *Helv. Chim. Acta*, 1931, **14**, 285; B., 1931, 553
31. *Aufbau der hochpolymeren organischen Naturstoffe*, Leipzig, 1930, p. 75.
32. *Z. angew. Chem.*, 1923, **36**, 242.
33. *Ann.*, 1840, **35**, 301.
34. *Chem. and Ind.*, 1933, **52**, 608.
35. *Mod. Plastics*, 1936, **14**, No. 2, 33; 1937, **15**, No. 2, 24, 74; 1938, **16**, 32; and *Ind. Eng. Chem.*, 1939, **31**, 178.
36. *Chem. and Ind.*, 1935, **54**, 102.
37. B.P. 151,016 (1920).
38. B.P. 179,094 (1921) and 181,014 (1921).
39. *The Chemical Age*, 1934, p. 537.
40. B.P. 248,477 (1926).
41. *J. Amer. Chem. Soc.*, 1934, **56**, 204.
42. *Kolloid-Beihfte*, 1933, **37**, 343.
43. *Ind. Eng. Chem.*, 1938, **30**, 1021.
44. B.P. 437,642; B., 1936, 100.
45. B.P. 437,361; B., 1936, 100.
46. *Chem. and Ind.*, 1940, **59**, 434.
47. *Text. Col.*, 1939, **61**, 17.
48. *J. prakt. Chim.*, 1856, **69**, 85.
49. *Ann. chim. phys.*, 1863 (3), **67**, 313.
50. *J.S.C.I.*, 1901, **20**, 1075.
51. *Ibid.*, 1926, **45**, 190 r.
52. *Ind. Eng. Chem.*, 1919, **11**, 1031, 1116.
53. *Ibid.*, 1934, **26**, 17.

54. *Ind. Eng. Chem.*, 1933, 25, 613.
55. *Chem. Rev.*, 1931, 8, 353.
56. *Ind. Eng. Chem.*, 1930, 22, 590.
57. *Ibid.*, 1933, 25, 971.
58. *Ibid.*, 1936, 28, 1150.
59. *Industrial Chemist*, 1927, 3, 431.
60. *J. Amer. Chem. Soc.*, 1928, 50, 1160.
61. *Chem. Age*, 1930, 41, 397.
62. *Ind. Eng. Chem.*, 1933, 25, 645.
63. *Ibid.*, 1936, 28, 1130.
64. *Les carbures d'hydrogène*, p. 901.
65. *Ind. Eng. Chem.*, 1934, 26, 1008.
66. *Ber.*, 1931, 64, 1493.
67. *Chem.-Ztg.*, 1912, 36, 199.
68. G.P. 281,687 (1912).
69. *Ann. Reports, S.C.I.*, 1938, 23, 453.
70. *Ind. Eng. Chem.*, 1934, 26, 561.
71. *Ibid.*, 1936, 28, 1123.
72. *Ibid.*, 1940, 32, 64.
73. *Ibid.*, 1940, 32, 315.
74. *J. Amer. Chem. Soc.*, 1907, 37, 34.
75. *J. chim. phys.*, 1921, 18, 333.
76. *Ind. Eng. Chem.*, 1933, 25, 997.
77. J. W. Cornford and Imp. Chem. Ind. Ltd., B.P. 407,753; B., 1934, 617.
78. *Ind. Eng. Chem.*, 1936, 28, 635.
79. *Ibid.*, 1936, 28, 267.
80. Röhm and Hass, A G, U.S.P. 2,067,580 (1937).
81. Du Pont, U.S.P. 2,063,315 (1936).
82. I.C.I., B.P. 474,242 (1937).
83. *Brit. Plastics*, 1937, 9, 5, 55.
84. G.P. 401,720 (1924); B., 1925, 216.
85. *Helv. Chim. Acta*, 1935, 18, 491.
86. *Oester. Chem. Ztg.*, 1921, p. 16.
87. G.P. 335,914 (1921).
88. Thomas and Hochwalt, U.S.P. 1,836,629 (1931); B., 1932, 902.
89. Thomas and Carmody, *Ind. Eng. Chem.*, 1932, 24, 1125.
90. U.S.P. 1,766,927 (1930).
91. *Ind. Eng. Chem.*, 1936, 28, 1174.
92. *Ibid.*, 1940, 32, 304.
93. *Ibid.*, 1930, 22, 1180.
94. U.S.P. 1,855,016 (1932).
95. *Ind. Eng. Chem.*, 1928, 20, 597.
96. *Brit. Plastics*, 1934, 6, No. 63, 99.
97. U.S.P. 1,732,453 (1929).
98. *J.S.C.I.*, 1931, 50, 191 T.
99. Patrick and Mnookin, B.P. 302,270 (1928).
100. *Ind. Eng. Chem.*, 1938, 30, 476.
101. *Kunststoffe*, 1931, 21, 49.
102. *J. Amer. Chem. Soc.*, 1931, 53, 4203.
103. *Ind. Eng. Chem.*, 1934, 26, 33.
104. *Ibid.*, 1932, 24, 563.
105. L. Lowen and H. K. Benson, *Ind. Eng. Chem.*, 1934, 26, 1273.
106. Sweeney, *Iowa State Coll., Bull.*, 1924, 73.
107. U.S.P. 1,917,038 (1933).
108. *Ibid.*, 1,725,791-97 (1929).
109. *Ind. Eng. Chem.*, 1936, 28, 275.
110. *Chem. and Ind.*, 1938, 57, 3.
111. *Ibid.*, 1936, 28, 1130.
112. *Ind. Eng. Chem.*, 1937, 29, 595.
113. E. A. Bevan and J. J. Siddie, *Trans. Oil and Colour Chem. Assoc.*, 1932, 15, 177
114. *Off. Digest*, 1940, 199, 397.
115. *Chem. Soc. Annual Reports*, 1927, 24, 124; 1929, 26, 159.
116. *Helv. Chim. Acta*, 1932, 15, 1300, and L. F. Fieser and W. P. Campbell, *J. Amer. Chem. Soc.*, 1935, 60, 159.
117. U.S.P. 1,245,975; 1,245,976; 1,245,978; 1,245,979; 1,245,983; 1,245,984 (1917).
118. *Brit. Plastics*, 1936, 7, 516.
119. *Ind. Eng. Chem.*, 1938, 30, 346; *Brit. Plastics*, 1938, 10, 248.
120. *Nature*, 1936, 137, 803; *J. of Textile Inst. (Eng.)*, 1936, 27, 281.
121. *Ind. Eng. Chem.*, 1938, 30, 1236.
122. *Industrial Chemist*, 1925, 1, 250.
123. *Brit. Plastics Year Book*, 1932, p. 31.
124. *Ind. Eng. Chem.*, 1934, 26, 819.
125. *Ibid.*, 1940, 32, 31.
126. *Ann. Reports, S.C.I.*, 1939, 24, 403.
127. *Ind. Eng. Chem.*, 1934, 26, 26.
128. B.P. 1313 (1865).
129. *Compt. rend.*, 1865, 61, 484.
130. *Ber.*, 1879, 12, 2059; 1881, 14, 1290.
131. B.P. 9676 (1894).
132. U.S.P. 733,729 (1903); 828,350 (1905).
133. G.P. 322,586 (1912).

134. *Chem. and Ind.*, 1940, **59**, 329.
135. *Die Cellulose*, 1923, p. 201.
136. *Brit. Plastics*, 1935, **6**, 433.
137. *Ind. Eng. Chem.*, 1936, **28**, 1144.
138. *Ibid.*, 1940, **32**, 464.
139. *Chem. and Ind.*, 1934, **53**, 761.
140. *Ind. Eng. Chem.*, 1934, **26**, 123.
141. *Brit. Plastics*, 1933, **4**, 446.
142. *Industrial Chemist.*, 1937, **13**, 486.
143. *Trans. Soc. Chem. Ind.*, 1938, **57**, 327.
144. *Chem. and Ind.*, 1935, **54**, 246, and *Brit. Plastics*, 1938, **9**, 452.
145. *Chem. Met. Eng.*, 1935, **42**, 408, and H. Barron, *Chemical Age*, 1939, 441.
146. *Brit. Plastics*, 1936, **7**, 190.
147. *Ibid.* 452.
148. *Chem. and Ind.*, 1938, **57**, 607.
149. B.P. 417,948 (1934); B₃ 1935, 34.
150. B.P. 461,649 (1937).
151. B.P. 461,650 (1937).
152. B.P. 484,476 (1938).
153. *Modern Plastics*, 1937, **15**, No. 2, 17.
154. *Ibid.* 38.
155. B.P. 491,686 (1938).
156. B.P. 492,642 (1938).
157. *J. Roy. Soc. Arts*, 1940, **88**, 673.
158. *Nature*, 1939, **143**, 785.
159. *The Industrial Chemist*, 1940, **16**, 120.
160. *Ind. Eng. Chem.*, 1937, **29**, 380.
161. H. M. Langton, *Food*, 1941, **10**, 113.
162. *The Industrial Chemist*, 1940, **16**, 133.
163. *Chem. and Ind.*, 1939, **58**, 180.
164. *Reports on Progress in Physics*, 1938, **5**, 64.

CHAPTER II

THE PROTEIN AND CELLULOSIC PLASTICS

By V. E. YARSLEY

ALTHOUGH strictly speaking it may be deemed incorrect to classify these two groups of plastics together, they have sufficient in common to warrant this being done. Both are derived from natural raw materials, the one of animal origin and the other of vegetable origin. Both include pioneers of the pre-World War days, although the use of these materials has very considerably increased in recent years in spite of the ever-increasing competition of the newer plastics. The casein and cellulosic plastics belong to the thermoplastic family, although the former actually enter commerce in a formalized condition very much resembling the synthetic resinoid plastics of the bakelite and amino-plastic types. The soya-bean plastics by contrast are thermo-hardening, and are as yet in the early stages of commercial development.

1. THE CASEIN PLASTICS

(a) The Nature and Origin of Casein.

Casein is the main protein of natural cow's milk, in which it occurs as a calcium compound forming approximately 3 per cent. of the whole. It belongs to the group of proteins known as phosphoproteins. Casein is a pure white, tasteless, odourless, non-crystalline solid. As usually prepared, it is a fine friable powder, quite stable when reasonably dry, but if moist it undergoes putrefactive decomposition. It is in equilibrium with an atmosphere of average humidity of 7 to 8 per cent. moisture, whilst heating above 90° causes loss of weight and decomposition. The specific gravity of casein is given as 1.259, and according to W. L. Davies¹ and L. A. Rogers² it contains 53.5 per cent. of carbon, 7.04 to 7.13 per cent. of hydrogen, 15.8 per cent. of nitrogen, 0.71 per cent. of phosphorus, 0.72 per cent. of sulphur, and oxygen by difference 22.14 to 23 per cent.

Casein is insoluble in water, alcohol, and most neutral organic solvents, and it is not readily wetted by water or aqueous solutions unless it contains traces of moisture. Strong acid solutions hydrolyse casein, but cold, dilute, inorganic acids have no action on it, although it is soluble in them and in the common organic acids, acetic, formic, and lactic. Casein dissolves readily in dilute aqueous solutions of alkaline hydroxides, and in dilute solutions of their soluble carbonates and bicarbonates.

Supplies of casein are widespread, although the main source of the best commercial casein for plastics manufacture is France. Since the fall of France in June 1940 this material has not been available

to the British industry, but alternative supplies have been obtained from the Argentine. Whilst this does not equal the French material in quality, it is being improved since British technicians have actively co-operated in its production in the Argentine. Casein is also obtained from New Zealand, and it is claimed that this material is cleaner than that from France, but less soft. The different types of commercial casein, their preparation, varying composition, and physical properties, have been discussed by C. Porcher,³ and the conclusion is drawn that there are but two types of casein: that prepared by the rennet method, which is a double salt of calcium para-caseinate and calcium phosphate, and that prepared by the acid method, which is casein only. The latter may be transformed into the former, but the reverse reaction is not possible. W. Schubring⁴ has tabulated the world production, exports, and imports of casein by the various countries from 1933 to 1939. Total production was about 192, 175, 168, 129 million lb. for 1938, 1937, 1936, and 1935 respectively. Production in 1939 appears to have declined, but the volume of trade was greater.

Many methods have been devised for precipitating casein from milk, but so far as its commercial use is concerned, two general methods are in use: (a) precipitation by acid, (b) coagulation by the rennet enzyme, rennin. This latter acts on the calcium caseinate of milk, causing the separation of a jelly-like curd (cheese-curd, junket) and a clear greenish liquid, whey. Rennet can clot 400,000 times its weight of casein in milk, and Fenger⁵ showed that rennet will coagulate more than 2,000,000 times its weight of fresh milk in 10 minutes at 40°. The optimum temperature range for the action is 36–45°, the best result, a firm curd, being obtained at 41°. The more dilute the rennet the larger the time required, according to Porcher.⁶ This precipitate, formed by the action of rennin on casein solutions, is called 'paracasein'.

A recent article⁷ describes the modern production of casein in the United States by direct acidification with hydrochloric acid. But as acidification methods are not employed in the production of casein for the plastics industry, attention will be confined in these pages to the dry process in which rennet is employed.

The use of rennet to precipitate casein is described by W. H. Simmons.⁸ The milk is collected under clean, antiseptic conditions and is processed as soon as possible after collection. Care is taken to remove the cream as completely as possible, the skimmed milk being run into vats where it is steam-heated to 100° F. and the right quantity of rennet added during continuous stirring. The stirring is so adjusted that the grains of curd formed are the size of peas. On completion of the precipitation, the whey is run off, the curd washed three times with warm water, drained, pressed, and dried in trays at 110–115° F.

The casein thus produced should be in the form of clean, translucent, slightly yellowish grains, with only a very slight smell and taste. Powdered and boiled with water for one minute, the casein

granules should swell evenly but not coagulate. The ash content should be about 8 per cent., a low value indicating that the milk was not fresh enough when precipitated. The moisture content should be 10–12 per cent. A casein with low moisture content has been dried at too high a temperature and will be unsuitable for plastic manufacture. Rennet casein, further, is not completely soluble in alkalis, such as caustic soda solution, in contrast to the acid-coagulated variety.

The analytical valuation of technical casein is described by F. Baum,⁹ who says that the proportion of true casein substance is obtained after deduction of the fatty acid, neutral fat, ash, and water content of a number of commercial caseins. Variations in this figure show 3 to 4 per cent.

It is important that the fat content of casein for plastics manufacture should not exceed 2 per cent. This determination is made by the modified Werner-Schmidt method as described by Bray and Major,¹⁰ and depends on solution in hydrochloric acid followed by extraction, first with ether, then with petroleum ether.

(b) The Production of the Casein Plastic.

The transformation of casein grains by mastication under the influence of heat and pressure in the presence of moisture into a homogeneous plastic mass, which acquires hard, horn-like properties after treatment with formaldehyde, forms the basis of casein plastics manufacture.

Casein should be kept, but not for long periods, in a dry, well ventilated store until ready for grinding. This operation is preceded by coarse sieving, after which the casein travels to a 'kibbling' machine where it travels between two grooved rollers for preliminary reduction followed by grinding in a four-high roller mill. The product from the mill is passed to a purifier in which it is sifted or graded, and freed from light particles. The cleaned, sifted material, which should be of such fineness that all of it will pass through a 40-mesh sieve but tail on an 80-mesh, is finally passed through a magnetic separator.

The mixing takes place in a dough mixer, which is illustrated in Fig. 1, and normally to 100 kilos of casein, containing 10 per cent. moisture, are added 26 kilos of water. The water must be free from iron salts, and should either be freshly distilled or softened. For colouring purposes, where such is necessary, acid dyes are added, and these should be as fast to light as possible. The water is added to the mixer in the form of a spray, 15 minutes being occupied in the case of a charge of the size indicated, and the mixing continued thereafter for an hour.

Many additions to mixings have been suggested as aids to softening and transparency:^{9,10} only glycerine, to the extent of 2 per cent. of the weight of the casein, is desirable, but tricresyl-phosphate and methyl-diphenylamine aid the plasticizing and add translucency.

The mixture of casein, water, &c., is now ready for extrusion, an

operation performed in a horizontal screw extrusion press consisting essentially of a 4-6 in. diameter revolving screw fitted in a jacketed body with a feed hole at the back end, and a heated nozzle at the front. Over the feed hole is a hopper holding the moist casein, with a simple stirring and feed-regulating device. The body of the

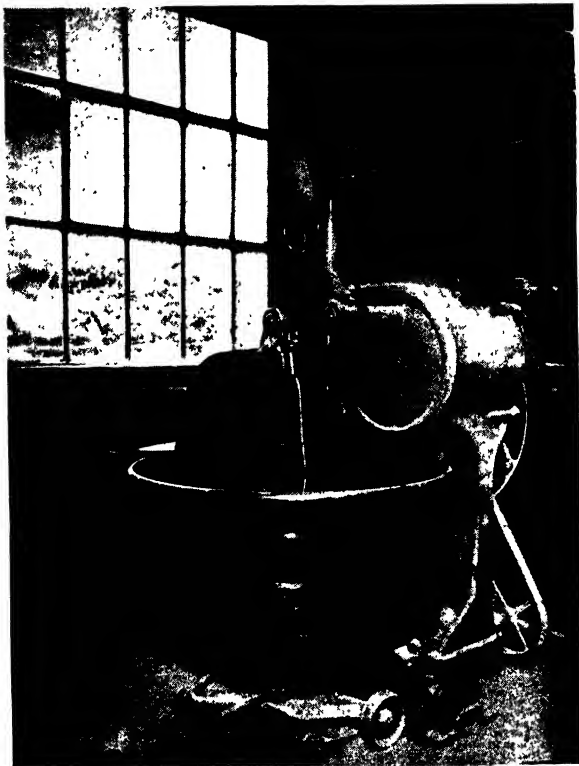


FIG. 1. An Artofex Mixer for Casein Plastic (as used at the works of Erinoid Limited)

machine which surrounds the screw is fitted with two separate jackets provided with steam and cold water supplies. At the front of the screw a perforated steel grid is fitted behind a nozzle, which can be changed to give various-sized rods, or fitted with a mandrel to produce tube.

The most important item in casein plastics plant is what Haupt¹³ calls the stuffer (i.e. the extrusion press), illustrated in Fig. 2. This conveys the casein as fed into it in the direction of the orifice, during which time the mass is compressed, masticated, and made uniform, and ejects it as a rod free from occlusions or impurities. The spiral conveyer tapers proportionately to the compressibility of the

materials. The rear end is water-jacketed and cold water prevents sticking of the particles or formation of air-pockets. The forward end and the steel sieve are warmed, and the nozzle is steam or electrically heated so that there is free flow of the homogeneous mass. At this stage the material is soft, like rubber, and then

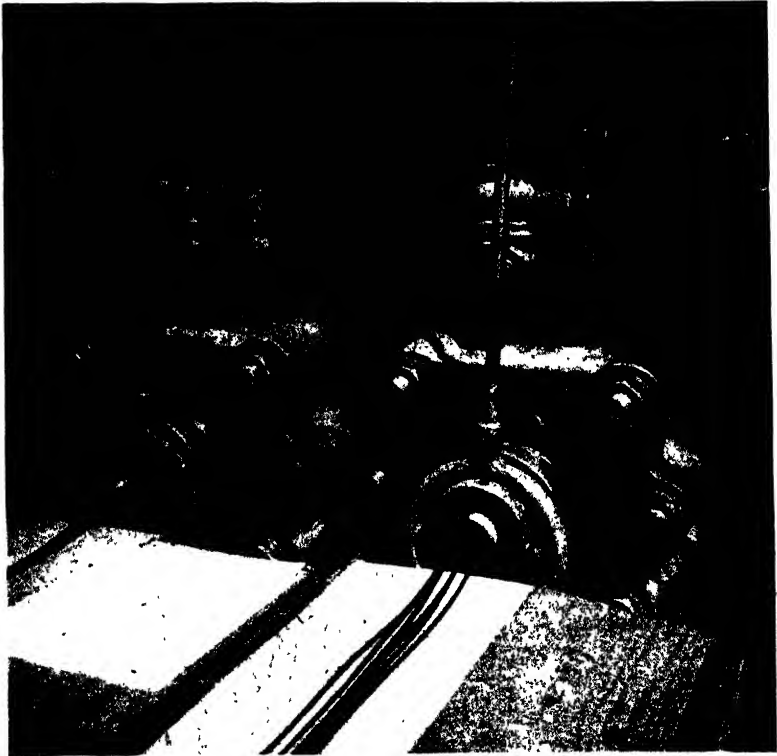


FIG. 2. The Extrusion of Casein Rod.
(By courtesy of Erinoid Ltd.)

gradually hardens to a firm material as it is extruded, and is conveyed away, cut to size, and cooled in water.

In front of each extrusion machine is a table covered by a belt which travels at a rather higher speed than that of the extruded rod. The rods are thus under slight tension so that they are kept straight.

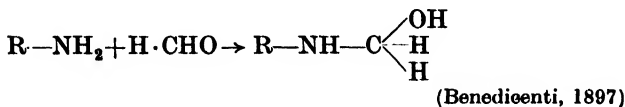
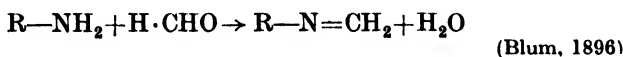
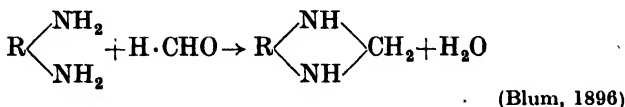
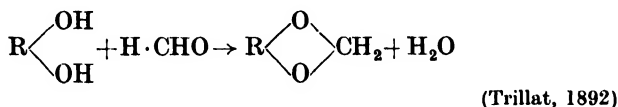
Mottled material resembling horn, tortoise-shell, &c., may be made either by using a double-screw type of extruder with a single nozzle, i.e. two separate mixings are thus fed into each screw, and, having been plasticized separately, meet and are extruded together through the nozzle,¹⁴ or alternatively a small quantity of coloured material

may be made and then pressed into a sheet direct from the powder. This sheet is cut up into pieces of about $\frac{1}{8}$ in. cube, dried somewhat, and added to a suitably coloured mixing base. The mixture is then extruded in the ordinary way.

For sheets two methods are used: the mixed coloured casein powder is spread in a suitably shaped mould and pressed, or the rods obtained by extrusion are cut into uniform lengths of suitable size; these are placed in moulds made of duralumin. The moulds are pressed in a multiple platen hydraulic press of standard type. The platens are heated to 180–190° F. and a pressure of about 600 lb. per sq. in. applied for 3 minutes followed by application of full pressure up to 2 tons per sq. in. for a further 3 minutes. Cooling by water now follows, cold water being passed through the platens for another 6 minutes while the pressure is maintained. On removal from the press the sheets are soft, but quickly dry in the air and become brittle.

(c) **The Hardening of the Casein Plastic.**

The casein plastic is hardened and rendered more or less water-proof by treatment with formalin. For this purpose 40 per cent. formaldehyde is diluted to 5–6 per cent. strength, weaker for thin sheets and stronger for thick sheets and rods. The treatment is carried out in brick tanks lined with cement, and through these the solution is kept in circulation by pumps, temperature maintained at about 65° F., the strength of the solution being maintained by suitable addition to the solution from day to day. The treatment varies from 2 days in the case of 2-mm. sheets to 2 months for rods of 25-mm. diameter. The material is now removed and washed with water to free it from adhering formaldehyde. During this curing the formaldehyde gradually soaks through the casein and the change which occurs, said to be in the nature of a condensation, has been variously explained, according to Simmond,¹⁵ by the following equations:



The formaldehyde treatment may be considered as a physical process of absorption and swelling, and a chemical one in which hydrogen in the amino group of the casein is replaced by methyl groups, i.e. condensation. These two processes are opposed in their tendencies, absorption with swelling, and condensation with shrinkage. An equilibrium is established, mainly dependent on the concentration of the formaldehyde, and differences of 0.5 per cent. may cause very considerable divergences in the time and effectiveness of the treatment.

Various alternative methods of treating casein for the production of hardened masses, plastics, &c., have been proposed, of which the following may be mentioned. Casein is mixed with 5 per cent. water and triethanolamine, or a mixture of the ethanolamines;¹⁶ casein is mixed with glyoxal or one of its homologues;¹⁷ alkaline solutions of casein containing a phenol are treated with an aldehyde in the presence of ammonia.¹⁸ Hardening of casein plastic masses¹⁹ will take place during hot pressing, if the mass contains compounds such as methyl-ureas and urethane which, at the temperatures employed yield formaldehyde and difficultly volatile substances which improve the properties.

(d) Drying and After-treatment.

The drying operation after formaldehyde treatment calls for little comment, but it is important to realize that casein plastics easily deform and shrink in drying, as indicated by some tests summarized later in this section. Rotation of casein rods while drying and suspension in a drying chamber are two methods practised in U.S.A. to prevent this shrinkage.²⁰

The usual practice is to take the washed crates containing the treated rods or slabs and place them in a drying-oven where they are subjected to a current of warm air at 80–115° F., the operation taking several days. In this country the moisture content is dried down to about 10 to 13 per cent. To counteract the warping which occurs during drying, rods are straightened by being softened in warm water and subsequently allowed to cool in wooden trays. For the sheets the practice is to put them in a press of the type already described and illustrated, where they are subjected to a pressure of about 250 lb. per sq. in. while being maintained at a temperature of 190° F.

Sheets and rods are polished in the usual type of polishing machine. The finished material can be easily turned and drilled and made into spectacle frames, buttons, umbrella handles, and fountain pens.

(e) The Manipulation of Casein Plastics.

Only rods and slabs are successfully produced on a large scale, and these must be mechanically cut in order to get objects of useful size. The scope of the casein plastics industry is therefore, for this

reason, more restricted than is the phenol-formaldehyde plastics industry. The manufacture of buttons probably accounts for the largest quantity of the casein plastics produced.

In the general manipulation of casein plastic the following operations are of importance:

Softening. The property of becoming softened when immersed in water is, as is well known, one of the useful characters of casein plastics, allowing them to be fashioned into definite shapes. The results obtained show that equilibrium is not rapidly attained: weight increases upwards of 20 per cent. in most cases, 30.6 per cent. being recorded in one test at the end of 21 days. Diameter increases by about 10 per cent. at the end of 21 days. Casein sheets, rods, and tubes may be softened by:

1. Plunging into hot water, preferably in a steam-bath or on a grid placed over boiling water.
2. Soaking in cold water for 12-24 hours.
3. Placing the material on a hot-plate, the temperature of which must be carefully controlled so as not to exceed 85-90°.
4. Placing in an oil-bath at 80-100°; the latter figure must not be exceeded.

Sawing. This can be carried out either by band or circular saw with fine teeth and rapidly revolving.

Moulding. The best results are obtained by careful cutting of the material to its final shape, heating in a suitable mould followed by progressive pressing as the material softens. In this way too great displacement of material is avoided.

The preparation of casein moulded products has recently been patented. It consists in taking the precipitate obtained by acidifying an alkaline solution of casein and a thermo-hardening alkyd-resin (preferably one modified with castor oil), and maintaining this in contact with aqueous formaldehyde. After freeing from water, acid, and formaldehyde the product is ground and can be moulded.²¹

Efforts are now being made to produce films from casein. One such method uses dried degreased casein, which is brought into colloidal suspension in an alcoholic dispersion liquid of low density and rapid evaporation rate, by means of an alkaline salt.²² The solution is oxidized by hydrogen peroxide, the alkaline caseinate is coagulated under controlled conditions by the addition of hexamethylenetetramine and poured in a thin layer on a surface yielding strong impermeable films containing upwards of 80 per cent. casein.

Another method of manufacturing transparent casein films is to take a 15 per cent. solution of casein, filter under high pressure to remove insoluble mineral salts, &c., add glycerine as plasticizer, and treat with formaldehyde before or after coating on the base, and drying.²³

Various special compositions have been suggested for use in the manufacture of casein plastics. R. Greenhalgh proposed a mixture of casein and less than half its weight of a resole, e.g. a diphenylol-propane-formaldehyde condensation product.²⁴ This horn-like

material is mouldable. It has also been proposed to incorporate with casein liquid hydro-aromatic or aliphatic hydro-aromatic amines or aliphatic amines containing hydroxyl groups.²⁵

(f) Properties and Applications of Casein Plastics.

Casein plastics used in attractive colours in sheet and rod form, and for simple pressed shapes, often develop faults if shrinkage in warm, dry atmospheres be not properly considered during design. In some tests described by Halls,²⁶ casein rods of various colours, of specific gravity at 15.5° varying from 1.32 to 1.45 and of ash content (determined by incineration) of 7 to 19 per cent., were conditioned for 18 hours at 75 per cent. humidity and 20° before being tested. The loss in weight and decrease in diameter of these rods upon exposure to dry heat for 6 hours at 110° were then determined. Loss in weight varied from 2.7 per cent. to 4.9 per cent., and the decrease in diameter from 0.5 per cent. to 2.9 per cent. The same specimen rods, similarly conditioned as above described, were immersed in water at 20° and the increase in weight and diameter respectively determined at intervals of 1 day, 7 days, 21 days.

Erinoid (a casein plastic manufactured in this country by Erinoid Ltd. of Stroud) is available in sheets 16 in. × 20 in., 2 mm. to 20 mm. thick; rods, 2 mm. to 20 mm.; tubes, 8 mm. to 35 mm. It is supplied polished, unpolished, or trapped. It is slightly hygroscopic and is practically free from dielectric absorption; it carbonizes at 200°; it can be turned, drilled, and generally worked with the same ease as wood. Recommended conditions for moulding or shaping are a pressure of 1,500 lb. per sq. in. at 94–99°.

R. Dodd²⁷ has enumerated the properties of the British casein plastic 'Erinoid'. Specific gravity is given as 1.33–1.34, but age and atmospheric conditions may cause variation of this figure ranging over $\frac{1}{2}$ per cent. either way. At 130° discoloration of Erinoid is noticeable in cream and light colours, but this would pass unnoticed in black and other dark colours. Erinoid is non-inflammable and therefore cannot be said to have a flash-point in the ordinary sense of the word; it is somewhat hygroscopic and has a water absorption round 15 per cent. after 48 hours' immersion. Whilst this hygroscopicity enables casein plastic to be softened in hot water, and stamped, moulded, and pressure-polished, it limits its application in many directions. This disadvantage has to some extent been overcome by after-treatment of the plastic unit with a water-resistant coating. Attempts have also been made to increase the water resistance by chemical treatment. According to the Society of Chemical Industry in Basel,²⁸ a water-resistant benzoyl casein is prepared by treating casein with benzoyl chloride for 12 hours at 50–60° in pyridine, but there is no indication that this new material has attained any commercial success. Mixtures of casein with cellulose ether compositions have been recommended as offering increased water resistance by D. A. Rankin and Du Pont.²⁹ The use of casein/vinyl

resin mixtures for the production of fibres and films has been described by J. Selzer.³⁰ The properties of casein plastics can also be modified by suitable plasticization, a technique which has been reviewed by J. Delorme.³¹ A comprehensive survey of the elastic and plastic properties of rennet casein has been given by C. A. Cooper and P. G. T. Hand,³² and a more general review by R. Dodd.³³

Casein plastic works in all respects like horn and ivory, and it can be turned, drilled, polished, stamped, moulded, and engraved. According to Dodd, it has found its way into twenty to thirty different trades as an article of everyday use. Casein ranks among the most outstanding of the colour plastics and is widely used in the manufacture of buttons, cutlery, combs, spectacles, umbrella handles, fancy goods, electrical units, &c. In recent years, and particularly since the phenomenal advances made in the injection moulding of acetate plastic, casein has suffered severe competition in some of these fields. Casein plastic is playing an important part in our present war effort, and it ranks among the few of the pioneer plastics which also saw service in the World War of 1914-18. R. Dodd³⁴ has reported in this connexion that a feature of the past year has been the successful development of casein plastic material in its application to the production of small parts for the aircraft industry. This has entailed the overcoming of many difficulties which had for many years been regarded as insuperable.

REFERENCES

1. W. L. Davies, *The Chemistry of Milk*, Chapman & Hall, London, 1936.
2. L. A. Rogers, *Fundamentals of Dairy Science*, 2nd edit., Reinhold Publishing Corporation, New York, 1935.
3. C. Porcher, *Chim. et Ind.*, 1928, 19, 589, 809.
4. W. Schubring, *Int. Rev. Agric.*, 1940, 31, 224-30 s.
5. Fenger, *J. Amer. Chem. Soc.*, 1923, 45, 249.
6. C. Porcher, *Rev. Gen. Coll.*, 1929, 7, 260.
7. *Chem. Met. Eng.*, 1934, 41, 645.
8. W. H. Simmons, *Industrial Chemist*, 1930, 6, 206, 229, 297.
9. F. Baum, *Chem.-Ztg.*, 1928, 52, 517-18.
10. G. T. Bray and F. Major, *J. Soc. Chem. Ind.*, 1923, 42, 106 t.
11. W. H. Simmons, loc. cit.
12. *Ibid.*, 1933, 9, 193.
13. Haupt, *Chem. and Met. Eng.*, 1932, 39, 319.
14. *Ibid.*, 1933, 9, 193.
15. Simmond, *The Industrial Chemist*, 1930, 6, 206, 229, 297.
16. U.S.P. 1,772,131.
17. B.P. 279,863; B., 1929, 406.
18. B.P. 272,947; B., 1928, 615.
19. B.P. 268,804; B., 1928, 615.
20. *Chem. and Met. Eng.*, 1932, 39, 319.
21. U.S.P. 1,978,533; B., 1935, 915.
22. B.P. 383,069; B., 1933, 78.
23. B.P. 434,993; B., 1935, 1041.
24. B.P. 370,739; B., 1932, 1042.
25. B.P. 297,483; B., 1928, 869.
26. E. E. Halls, *Brit. Plastics Year Book*, 1936, pp. 24-61.
27. R. Dodd, *Brit. Plastics*, 1930, 1, 478.
28. S.C.I., Basel, Swiss P. 182,395.
29. E. I. Du Pont and D. A. Rankin, U.S.P. 2,030,226; B., 1937, 158.
30. J. Selzer, *Rusta*, 1940, 15, 18-20.
31. J. Delorme, *Rev. Gen. Mat. Plast.*, 1935, 11, 375-9.
32. C. A. Cooper and P. G. T. Hand, *Brit. Plastics*, 1939, 10, 572-7.
33. R. Dodd, *J. Inst. Plast. Ind.*, 1936, 5, 58-64.
34. R. Dodd, *Brit. Plastics*, 1941, 12, 250.

2. SOYA-BEAN PLASTICS

(a) The Soya Bean.

According to W. L. Burlison,¹ the soya bean is one of the oldest crops grown, and it was described in a Chinese book on materia medica, *Ben Tsao Gang Mu*, written by Emperor Shen-Nung 4,800 years ago. In China and Japan the soya bean has been of prime importance since ancient times, and in value and variety of uses is still the outstanding legume grown in those countries. The production of soya beans in Asia is concentrated in Japan, Korea, and two regions in the eastern part of China. Previous to 1908 the trade in soya beans was confined almost altogether to oriental countries, particularly China and Japan. Since then the usefulness of the soya bean has been more generally appreciated in other countries, and an important international trade has developed.

The plant grows to a height of about 3 ft., has an erect hairy stem, and leaves which are divided into three leaflets. The small flowers are violet or purple in colour, and grow in short sprays. They are followed by seed pods resembling those of sweet peas, which are about 2½ in. long, and generally contain two or three beans. The beans imported from Manchuria have a golden tint, whilst the Russian beans are more definitely yellow, but green, black, and brown varieties also exist.

Soya beans were introduced into the United States in 1804, yet a hundred years later there were very few grown outside the southern states. By 1919 the crop had reached a fairly uniform development in the area east of the Mississippi River and considerable prominence in New England and certain southern and western states. However, the total acreage of soya beans in the United States fluctuated noticeably, and by 1924 had decreased in the eastern part of the country, particularly in New England and New York. In 1924, twenty-two states produced the bulk of soya beans in the United States, the total crop of gathered beans being slightly above 5,000,000 bushels.

From 1924 to 1935, inclusive, production increased rapidly, figures for 1935 indicating a total of nearly 39,637,000 bushels of gathered beans. The more rapid increase of production has occurred in the corn-belt states, particularly in Illinois, Missouri, Indiana, and Iowa. In 1935 Illinois produced about one-half of all the beans crushed in America.

The soya bean (*Soja Max*) is a summer leguminous annual. Pods are from 1 to 2.5 in. long and contain from two to four seeds. The stems, leaves, and seed-pods are covered with short reddish-brown or grey hairs. The root tubercles are large and abundant. There are many varieties of soya beans and literally hundreds of types and strains.

With the exception of cowpeas and lespedeza, the soya bean is more acid-tolerant than any other legume crop grown in the corn belt where most of the commercial beans are produced. Cultivation of the crop is not complicated and is similar to that of corn. Soya

beans can be grown on the average corn-belt farm with the tools already in use for other crops. The combine, which threshes out the beans and leaves the straw on the land, has been a boon to the soya-bean grower as well as to the wheat producer; in Illinois there are about three thousand of these machines. Illinois averaged 18 bushels of soya beans per acre in 1935. Cost records reported by the Illinois Agricultural Experiment Station show that soya beans can be produced for 63 cents per bushel as an average for the three-year period 1931-3. These were low-cost years because of high yields and the advantages of harvesting with the combine.

The bean is practically free from starch and is therefore valuable in foods where the latter is not desired. The composition of the bean is substantially as follows:²

	<i>Per cent.</i>
Protein	40
Fat	20
Carbohydrate	20
Lecithin	2
Crude fibre	4
Ash	5
Starch	trace
Moisture	9
Enzymes (urease, diastase, &c.)	traces

The protein is all digestible; the carbohydrates are in the form of simple sugars; the ash is very rich in potash and phosphorus. Vitamins A, B, and D are also present.

In the United States by far the greater part of the production of this crop is used for forage for live stock on the farm. Of the part which finds its way into commerce, some of the beans are used as such, while some are ground into flour and used in such articles as bread, macaroni, sausage, chocolate, baby food, &c. Most of the beans which are not used for forage are crushed and the oil separated.

The composition of typical soya beans from various sources is given in the following table:¹

	<i>Protein</i>	<i>Oil</i>	<i>Water</i>	<i>Ash</i>	<i>Carbo- hydrates</i>	<i>Crude fibre</i>
	%	%	%	%	%	%
English						
'Jap' (1933)	46.26	13.00	8.32	4.97	22.89	4.56
„ (1934)	46.63	12.47	7.92	5.00	23.98	4.00
'C' (1933)	40.92	15.40	8.67	5.30	25.63	4.08
„ (1934)	41.64	15.15	8.04	4.70	25.97	4.50
'O' (1933)	40.09	16.96	7.89	5.15	24.57	5.34
„ (1934)	43.07	15.64	8.04	4.75	23.25	5.25
'J' (1933)	36.90	16.80	7.26	5.20	29.09	4.75
„ (1934)	37.66	15.95	8.09	5.03	28.90	4.37
U.S.A.						
Ito San	34.66	19.19	7.42	5.97	27.61	5.15
Midwest	35.54	19.78	8.00	5.85	26.30	4.53
Mammoth	32.99	21.03	7.49	5.01	29.36	4.12
Quelph	33.96	22.72	7.43	5.85	25.47	4.57
Manchurian Typical	36.68	17.50	12.00	4.92	24.10	4.80

The soya bean was introduced into the Western Hemisphere at the close of the Russo-Japanese war, and by 1907 shipments were being made to England. The imports of soya beans into this country, mainly for the production of oil, increased steadily from 1929, and in 1934 had reached from all sources a value of £1,005,477 for 177,194 tons, and attracted an *ad valorem* duty of 10 per cent. The growing importance of the soya bean and in particular the possibility of using it in the manufacture of plastics led to experiments being carried out to cultivate it in this country, and in 1934 20 acres were cultivated at Boreham in Essex by Fordson Estates Ltd., a concern associated with Ford Motors who pioneered the soya-bean plastics in America.³ This arose out of the untiring interest which Henry Ford took in bringing about a closer relationship between the American farmer and the automotive industry. Herbert Chase⁴ states that to date most of the soya beans used in the development of products suitable for use in manufacturing Ford cars and trucks have been raised on 12,000 acres of Mr. Ford's own farm-land. The chief use of the bean is in making oil which is employed in paint, shock-absorber fluid, and core oil, the latter required in the foundry. After the oil is extracted, however, there remains a residue called 'meal'. It is from the meal that the plastic is produced; or, to be more exact in statement, the meal becomes one important ingredient of the plastic.

It is estimated that it will require about 50,000 acres planted in soya beans per year to supply enough of the present soya products for one million cars annually. This acreage, it is stated, would provide about 825,000 gallons of oil suited for use in enamel, about 540,000 gallons for shock-absorber fluid, and about 200,000 for foundry core oil. Meal from the 12,000 Ford acres in soya beans, reduced to usable form in the Ford plant will, it is believed, be ample for the present schedule of plastic production. It is important from the Ford point of view that this much can be converted into plastics and, of course, it is another step in the plan to provide outlets for farm products.

(b) The Soya-bean Resinoid Plastic.

The initial stage in the production of the plastic is the purification of the raw material. This and the subsequent working up into the resinoid is given by R. L. Taylor.⁵

The plant obtains its soya beans from a rural mill where they are cleaned and weighed, having been received originally from the farmers' silos. Since the beans can be stored indefinitely as long as the moisture content is kept below 12 per cent., it is not difficult to maintain a constant supply throughout the year.

In the extraction building the beans enter a hopper on the second floor from which they are fed through a vertical wooden chute to the flaker. The flaker itself operates on the principle of a meat grinder, the body being a section of 12 in. pipe containing a revolving

steel core on which is a $\frac{1}{2}$ in. raised spiral. The beans are forced out through an adjustable slit at one end.

The flaked beans, along with a very small amount of oil that has been pressed out, are carried down from the flaker about 3 ft. in a closed vertical screw conveyor to the extractor proper. This is simply a piece of 12 in. standard steel pipe, 30 ft. in overall length, and set at an angle of 10 degrees with the horizontal. Operation is counter-current, the bean flakes being carried upward by a screw conveyor and the solvent running down the inclined pipe, or 'percolator' as the tube is called. Introduction of the solvent at a point about half-way down the tube allows the upper portion to be used as a steamer. There, by the use of a steam jacket and live steam, the last traces of solvent are vaporized from the meal. The steam and solvent vapours pass out of the upper end of the steamer to the solvent recovery system, while the wet, solvent-free meal is dropped to another steam-jacketed, inclined pipe which acts as a dryer. Carried down the dryer tube by means of a screw conveyor, the meal emerges through a barrel valve to an open conveyor, which takes it with a final moisture content of about 8 per cent. to steel drum containers.

At the present time the solvent used is hexane. Explosion and fire hazards have been reduced by open construction of the extraction building and complete enclosure of the solvent cycle, with the solvent at all times either in a cold and liquid condition or as vapour mixed with steam. The danger of a dust explosion also is lessened by the closed system. The total amount of hexane used in the system is only 200 gal., the rate of circulation being 270 gal. per hour or slightly more than half a gallon (3 lb.) per lb. of beans. The solvent loss is about 1 lb. per 100 lb. of beans.

The extraction process leaves a residual meal containing, on a dry basis, approximately 48 per cent. protein, the major portion of which is casein, 38 per cent. carbohydrates, 7 per cent. cellulose, and 7 per cent. ash. Making use of this high casein content, the production of moulding plastics consumes the greater part of the meal, requiring over 4,000,000 lb. per million cars. The chemistry of the soya-bean extraction has been reviewed by Horvath⁶ and further useful data have been given by M. Mashino.⁷

Early work in soya-bean plastics, according to Taylor,⁸ indicated that the pure casein-formaldehyde product displayed a decided tendency to absorb moisture over a period of time, often to the extent of 20 per cent., with a final result of serious warping and cracking. For that reason present practice calls for the addition of a certain amount of phenol, giving a composition of phenolic and casein-formaldehyde product which is both waterproof and durable. Although isolation and purification of the casein gives a higher grade plastic, the added expense has not been justified in view of the present satisfactory results obtained by using the whole meal. Since phenol is a good solvent for soya-bean meal, this method makes available both the casein for the formaldehyde reaction and the

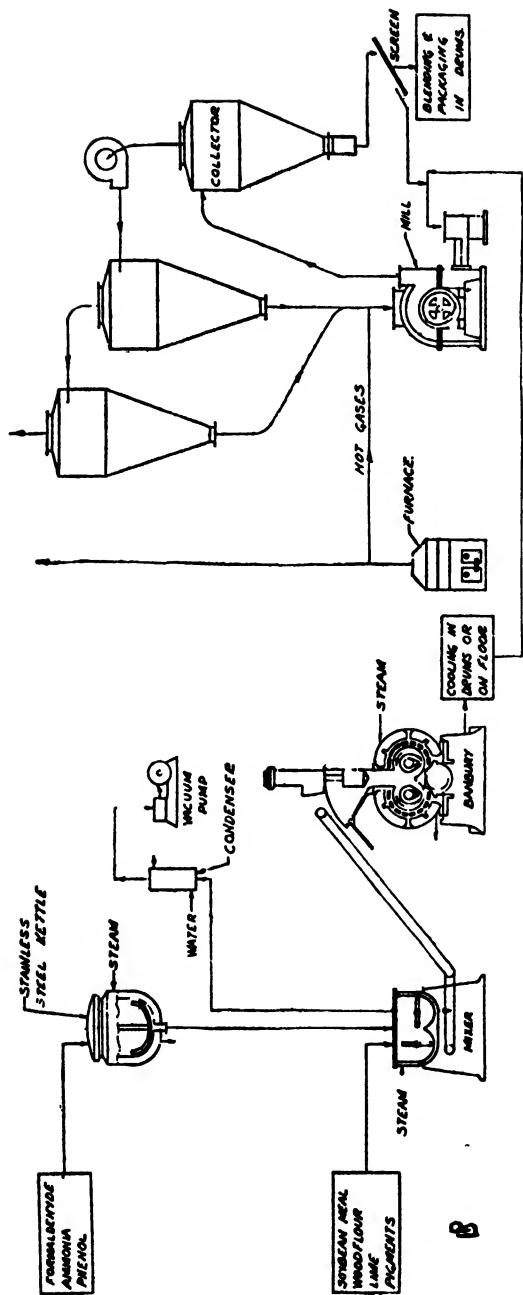


FIG. 3. Schematic diagram, showing the arrangement of equipment and the flow of material through it for producing the new Ford Soya-Bean Plastic. The following ingredients are employed in the quantities named:

Soya-bean meal, extracted	330.0 lb.	Alcohol	33.0 lb.
Wood flour	396.6 "	Pigments	75.0 "
Lime	26.3 "	Hexamethylenetetramine	26.3 "
Formaldehyde	250.0 "	Water	12.4 "
Ammonia	26.3 "	Stearic acid	4.1 "
Phenol	250.0 "	Zinc stearate	4.1 "

carbohydrates for filler, thus cutting the cost to a figure considerably lower than that of a straight phenolic plastic. Wood flour is used as additional filler.

The process for the manufacture of the actual soya-bean plastic is given by Taylor⁹ as follows:

The meal which comes into the plant is carried in a closed Redler conveyor from the storage room to an ordinary attrition mill where it is ground to a fine flour. Then the plastic batch is weighed into a jacketed Baker-Perkins mixer where it is worked for 2 hours at 200° F. and from 2 to 3 hours at a lower temperature. The weighing devices for the phenol, formaldehyde, and ammonia are each controlled automatically by a photo-electric cell arrangement capable of adjustment for any desired weight. The individual batches are varied from time to time to meet the different physical properties required in the various finished parts. A representative mixer batch consists of 330 lb. soya-bean meal, 250 lb. phenol, 250 lb. formaldehyde, 300 lb. wood flour, 30 lb. ammonia, and 25 lb. lime. The ammonia and lime serve as catalysts for the formaldehyde reaction.

Colouring pigment is added near the end of the mix, as is also a small amount of zinc stearate and stearic acid which serve as mould lubricants. Whereas during the mixing process the material lumps and becomes tough, the final contents of the mixer must be put through a Banbury internal mixing machine, such as is used in rubber compounding. This large machine, which is driven by a 200 h.p. electric motor, gives uniform density to the mass by its intense masticating action. From the Banbury the material goes to a Raymond kiln mill, where the temperature is kept below 150° F. in order to avoid premature curing. This mill is of the hammer type and is gas-fired, the hot air and gases carrying the ground material up through a vertical 12 in. sheet-metal pipe to a cyclone separator. There, after separation from the air stream, the dry material falls to a screen from which the oversize drops back to the grinder. The powder goes to a tumbler to obtain a uniform blend, and from there it is fed to the moulding machines. These are hydraulic presses which exert a force of 2,000 lb. per sq. in. and operate at a mould temperature of 360° F. The treatment of the material in that part of the processing between the mixing and blending is extremely important, every operation being closely timed so that the last stage of curing, which requires about 3 minutes, takes place in the presses. Premature curing would mean an un-mouldable plastic. The accompanying flow sheet given in Fig. 3 is for the manufacture of the soya-bean moulding compound as carried out at Ford's River Range plant.¹⁰

(c) The Soya-bean Plastic.

As has been pointed out by Beckel¹¹ and his co-workers, the plastic produced as above is of a mixed type and in it the soya

66 THE PROTEIN AND CELLULOSIC PLASTICS

meal plays the secondary role of a modifier, the main essential being the phenol-formaldehyde condensation resinoid. They point out that although it has been claimed¹² that soya-bean or other vegetable proteins can form the base for the manufacture of a number of

Moisture content	Initial thickness		Final thickness		Coefficient of plastic flow
	%	in.	mm.	in.	
<i>Soya-bean extracted meal</i>					
2.02	0.238	(6.045)	0.223	(5.664)	0.063
2.61	0.237	(6.020)	0.199	(5.055)	0.160
3.00	0.223	(5.664)	0.160	(4.064)	0.283
4.09	0.240	(6.096)	0.133	(3.378)	0.446
5.27	0.236	(5.994)	0.126	(3.200)	0.466
5.77	0.229	(5.817)	0.098	(2.489)	0.572
6.74	0.231	(5.867)	0.089	(2.261)	0.615
7.82	0.222	(5.639)	0.083	(2.108)	0.626
10.94	0.253	(6.426)	0.079	(2.007)	0.687
10.94	0.262	(6.655)	0.077	(1.956)	0.706
<i>Commercial soya-bean protein</i>					
2.11	0.208	(5.283)	0.199	(5.055)	0.043
2.71	0.189	(4.801)	0.178	(4.521)	0.058
4.11	0.166	(4.216)	0.114	(2.896)	0.313
4.37	0.209	(5.309)	0.125	(3.175)	0.402
6.61	0.187	(4.750)	0.088	(2.235)	0.529
9.65	0.224	(5.690)	0.075	(1.905)	0.665
<i>Soya-bean expeller meal</i>					
2.14	0.127	(3.226)	0.107	(2.718)	0.157
3.44	0.138	(3.505)	0.077	(1.956)	0.442
4.22	0.103	(2.616)	0.063	(1.600)	0.388
7.49	0.188	(4.775)	0.058	(1.473)	0.691
<i>Zein</i>					
0.00	0.139	(3.531)	0.137	(3.480)	0.014
0.67	0.140	(3.556)	0.138	(3.505)	0.014
2.57	0.130	(3.302)	0.110	(2.794)	0.154
5.34	0.141	(3.581)	0.071	(1.803)	0.496
9.48	0.159	(4.039)	0.039	(0.991)	0.754*
<i>Rennet casein</i>					
4.92	0.199	(5.055)	0.192	(4.877)	0.035
5.02	0.278	(7.061)	0.257	(6.528)	0.076
5.79	0.142	(3.607)	0.116	(2.947)	0.183
6.38	0.151	(3.835)	0.111	(2.819)	0.265
6.56	0.171	(4.343)	0.124	(3.150)	0.275
7.98	0.151	(3.835)	0.097	(2.464)	0.358
7.98	0.132	(3.353)	0.086	(2.184)	0.348

* Flow too great to be measured by this method with the equipment used.

plastics ranging from celluloid to rubber-like material, none of these claims has been substantiated by successful industrial production. These investigators have prepared plastics from soya-bean meal and protein and have compared these with those prepared from other protein materials.

Two different types of plastic were obtained, one by the addition of water which resembles the casein plastic, and the other a zein-like plastic obtained when the moisture content was reduced below 5 per cent. It was pointed out that the promotion of the large-scale uses of soya-bean meals for such plastics would be contingent upon the development of a material as free as possible from the disadvantages of casein and in particular of its high hygroscopicity. This work showed, however, that contrary to early reports, and contrary to the known properties of other known protein materials, the soya bean possessed flow properties at reduced moisture contents. The results of these investigations are collected in the table on p. 66, which gives the flow measurements on the various protein plastics at varying moisture contents.¹³

The authors state that casein, the only animal protein examined, shows marked differences in plastic behaviour from the other proteins.

The zein-type plastic produced from soya-bean meals and protein of less than about 5 per cent. moisture content is of no great commercial value in itself. Although it comes finished from the die and does not shrink or warp excessively, as in the case of the casein-type plastics, it is very hygroscopic and inclined to be rather brittle. Its importance lies in the new field of possibilities it opens for the development of a new line of mouldable resinous plastics. Since the material is thermoplastic and not dependent upon water for plasticization, it should be possible to work into it water-resistant plasticizers or reactants which would increase its thermoplasticity at the same time and render it reasonably impervious to water. Up to the present it has not been possible to do this in the field of protein plastics because water was considered essential for plasticization.

(d) Action of Hardening Agents on Soya-bean Plastics.

The soya-bean plastics share the disadvantage of the other protein plastics that they must be hardened or tanned to render them suitable for most industrial applications. The process is a long one and may take from 1 to 6 weeks, with a similar period for drying and seasoning. Numerous attempts have been made to avoid this by adding salts to the soft plastic to facilitate the subsequent penetration of the hardening agent. The action of hardening agents on protein plastics has been investigated by G. H. Brother and L. L. McKinney,¹⁴ and the results of the comparative water absorption of various plastics after treatment with formaldehyde or furfural which they obtained are given in the following table:¹⁵

Material	Water absorption, per cent.			
	Formaldehyde-treated		Furfural-treated	
	24 hours	48 hours	24 hours	48 hours
Soya-bean expeller flour	Disintegrated	Disintegrated	57.1	59.3
Soya-bean extracted flour	"	"	51.7	52.0
Soya-bean gamma protein	53.8	56.7	56.9	56.1
Soya-bean protein 70	Disintegrated	Disintegrated	39.4	50.1
Soya-bean alpha protein	10.0	17.9	37.4	37.6
Rennet casein	14.8	22.7	25.0	33.9
Lactic acid casein	10.7	14.6	24.6	36.5
Zein*	31.5	34.7	23.0	..

* Zein without treatment: 17.0 per cent. in 24 hours, 30.1 per cent. in 48 hours.

They conclude that solvent-extracted soya-bean meal and the commercial products, gamma soya-bean protein and soya-bean protein 70, present some possibilities when hardened with furfural. The plastic will have to be limited to black or very dark colours, but it is well knit, strong, and free-flowing, and the raw materials are very low in cost. The water absorption is too great for some applications, but there are indications that it can be corrected fairly easily by proper study. It has been found that a small percentage of aluminium stearate in the plastic mixture reduces the water absorption sharply.

Brother and McKinney have carried this work a step farther and have investigated the effect of seventy commercially available plasticizers on formaldehyde-hardened casein plastic.¹⁶ The study was conducted primarily from the effect of such additions on the plastic flow and water resistance of the plastics. They found that the polyfunctional alcohols gave positive results, and of these ethylene glycol was the best. The primary monohydric alcohols, esters, ketones, and oils gave most definitely negative results. Ethylene glycol improved the plastic flow of the material apparently as a true plasticizer, and this material may be rendered thermo-setting by heating. On the other hand, ethylene glycol increased the water absorption from 10 to 21 per cent. Oleic acid and aluminium stearates in admixture with ethylene glycol reduced water absorption more than other agents examined. Oleic acid is a sapogenic found in grape skins, olive leaves, and clove buds, and extracted by suitable solvents from grape pomace.

(e) Applications of Soya-bean Plastics.

As already mentioned, what may be termed the true soya-bean plastics do not appear to have attained much commercial importance, and this is no doubt due to the early success of the protein/resinoid plastic such as is typified by the Ford product. The latest work of Brother¹⁷ has, however, shown that a good line for commercial development is in the modification of the properties

of the hardened protein plastic material by the incorporation of compatible resin or compatible moulding compounds. In the past this has not been possible, but the thermoplastic-hardened protein material used has proved an ideal base for such development work.

REFERENCES

1. W. L. Burlison, *Ind. Eng. Chem.*, 1936, **28**, 772-6.
2. J. B. Phillips, *Chem. and Ind.*, 1934, 627.
3. *Oil and Col. T J.*, 1935, 1154-6; see also *The Soya Bean: Its History, Cultivation (in England) and Uses*, Elizabeth Bowbridge, Oxford Univ. Press, London.
4. H. Chase, *Brit. Plastics*, 1936, **7**, 516.
5. R. L. Taylor, *Chem. Met. Eng.*, 1936, **43**, 172-6.
6. A. A. Horvath, *Chem. and Ind.*, 1937, **56**, 735-8.
7. M. Mashino, *J.S.C.I.*, 1935, **56**, 236 T-238 T.
8. R. L. Taylor, loc. cit., 175.
9. R. L. Taylor, loc. cit., 176.
10. H. Chase, *Brit. Plastics*, loc. cit.
11. A. C. Beckel, G. H. Brother, and L. L. McKinney, *Ind. Eng. Chem.*, 1938, **30**, 436-40.
12. Satow, U.S.P. 1,245,975-6; 1,245,979-80.
13. A. C. Beckel, &c., loc. cit., 439.
14. G. H. Brother and L. L. McKinney, *Ind. Eng. Chem.*, 1938, **30**, 1236-40.
15. Loc. cit., p. 1240. Cf. also A. K. Smith and H. J. Max, *Ind. Eng. Chem.*, 1940, **32**, 411-415.
16. G. H. Brother and L. L. McKinney, *Ind. Eng. Chem.*, 1939, **31**, 84-7.
17. Loc. cit., 87.

3. CELLULOSE PLASTICS

THE NATURE AND STRUCTURE OF CELLULOSE

Cellulose is the non-nitrogenous constituent of all plant walls and in one of its many available forms provides possibly the most widely used raw material in the service of man. The cotton hair or linters has the highest cellulose content, round 90 per cent., whilst in bast fibres, wood, and cereal straws the content varies from 30 to 60 per cent. For many years the cellulose-using industries paid attention mainly to the more pure celluloses, but in recent years the possibilities have been realized of the vast quantities of ligno-celluloses and the like, which hitherto have either been burnt or returned to the earth as fertilizer. During the past few years the cellulose content of many of the widely distributed vegetable products has been examined. I. Miura¹ has examined Philippine and North Borneo woods which yield a maximum of 56.6 per cent. and an α -cellulose of 79 per cent. on the total cellulose. S. Hermanowicz² has shown that hemp straw and fibre contain respectively 37-55 per cent. and 71.5-77.5 per cent. of cellulose. Some interesting data showing the practical possibilities of gas chlorination in cellulose manufacture have been published by U. Pomilio,³ whose name is now widely associated with this process.

In the manufacture of cellulose derivatives for the production of plastics, lacquers, and rayon only the most pure celluloses are used in the form of refined cotton linters, paper, or wood pulp. Market conditions exert a marked influence on what may be termed production tendencies. At one time only cotton linters or high-quality paper tissue was used, but with the production of pulps of high α -cellulose content at an attractive price these materials gained in

popularity. When the price of pulp advanced the change came again in favour of cotton linters, and the present indications are that they will continue so.

Cotton linters are the short fibres and undergrowth which remain on the seeds after the main staple fibres have been removed by the 'ginning' process. The properties of the linters vary considerably according to the method of delinting applied, and according to B. T. Ardashev⁴ the latest method employs gaseous hydrochloric acid. General accounts of the production and utilization of cotton linters have been given by W. D. Munson,⁵ and A. J. Hall,⁶ whilst Wanda K. Farr⁷ has recorded experimental work on the nature and structure of the cotton hair.

A general idea of nature and structure of cellulose is an essential preface to any consideration of the production of cellulose derivatives, and it emphasizes that above all the cellulose unit is a delicate one so that every care must be taken to avoid its destruction from the initial stages up to the finished plastic.

Cellulose belongs to the chemical family known as carbohydrates and contains carbon, hydrogen, and oxygen, having an empirical formula $(C_6H_{10}O_5)_n$, where n represents not only an unknown degree but manner of aggregation. It is a polyhydric alcohol and contains three hydroxyl groups per C_6 unit, and as with ordinary alcohols it can form esters and ethers by the replacement of one or more of these groups. Whilst the cellulose esters have been known for over a hundred years, it was not until the beginning of the present century that cellulose ethers were produced commercially.

The elucidation of the structure of cellulose has provided a fruitful field for chemical research for many years, and there can be few chemical substances which have attracted so much attention. Much of the earlier work has now been discounted, and to-day we are in possession of a concise picture of the cellulose unit. As a typical colloid cellulose does not conform to precise molecular limitations, and the working unit is called the micelle. In its most simple form the micelle structure implies an arrangement in which the micelles may be likened to the bricks in a wall overlapping each other in much the same manner. They are held together by micellar forces, to form the fibrils which are the most elementary constituents of the natural fibre which can be detected under the microscope. Since X-ray diagrams account for only 75 per cent. of the cellulose existing in the crystalline state, Herzog⁸ concludes that the remainder is the cementing material. Within the micelle is the chain molecule, the fundamental unit of which has been proved to be the glucose anhydride residue. This in turn has been shown to be a ring structure consisting of five carbons and one oxygen, the units being linked through bridge oxygens in the 1·4 positions. The arrangement of the micelles and the chain molecules within the micelle have been shown diagrammatically by Clark.⁹ The length and number of the chains which go to make the micellar bundle has been the subject of considerable controversy for many years, but the work of W. N.

Haworth and his school on the methylation of the end groups has done much to establish our accurate picture of the unit structure of cellulose. In a recent epitome Haworth¹⁰ has shown that natural cellulose is a molecular aggregate of chains the minimum length of which could not be less than 200 glucose units, and that these chains are joined end to end in a large physical molecule; that the molecular aggregate may be expected to take account not only of an aggregation which increases the length of the chains but also of the forces which effect aggregation laterally between adjacent chains.

THE CELLULOSE ESTERS

(a) Nitrocellulose.

The pioneer and, from the viewpoint of plastics and lacquers, still the most important ester of cellulose is nitrocellulose, which was prepared by Schoenbein in 1845 by treating cellulose with a mixture of nitric and sulphuric acids. Concentrated nitric acid (d. 1.5) will nitrate cellulose, but in practice the mixed acids are always used. The vital function of the water content of the mixed acids in influencing the nitrogen content of the resulting ester was recorded by Lunge and Bebic¹¹ as long ago as 1901.

There is evidence that twelve definite nitrates have been prepared, and on the basis of the glucose residue the tri-nitrate should contain 14.2 per cent. of nitrogen, the di-nitrate 11.1 per cent., and the mono-nitrate 6.8 per cent. All cellulose nitrates are inflammable, and those esters with a nitrogen content exceeding 13.1 per cent. are unstable. Esters containing 11 to 13.4 per cent. of nitrogen are 95–100 per cent. soluble in acetone; ether/alcohol (2:1) solubility is recorded over the range 11–12.5 per cent., whilst 50–100 per cent. solubility in ethyl alcohol is found with a nitrogen content of 11–12 per cent. The lower esters with nitrogen content 10.2–11 per cent., sometimes called 'Xyloidin' in England and 'Pyroxylin' in America, are characterized by their solubility in camphor/alcohol, and are mainly used in the manufacture of celluloid. The middle range 11.2–12.4 per cent., the ether/alcohol soluble collodion cottons, are mainly used in the manufacture of lacquers and films, whilst above this range 12.4–13 per cent. are the explosive gun-cottons.

The nitration of cellulose has provided a fruitful field for chemical research for the past half-century, and the methods for its commercial production, which were reviewed by Nathan,¹² fall into three classes: (1) pan nitration in which the cotton is dipped directly into the acid in separate earthenware 'pans', (2) nitration in centrifugals, and (3) the displacement process. Pan nitration is now only of historical interest since it gave place to the more logical nitration in centrifugals which gives a high output per man, although the plant cost and maintenance is high. The displacement process differs from the others mainly in the method of separation of the acid from the cotton. This is done by allowing the water to enter slowly from the top of the nitrating pan whilst the spent acid is removed

at the same rate from below. The advantages of the displacement process are economy of acid and output. A useful general account of improvements in the manufacture of nitrocellulose was given by Partridge,¹³ whilst Tomonari¹⁴ has traced the connexion between the composition of the mixed nitric/sulphuric bath and the nitrogen content of the resulting esters. He has shown that the products derived from the nitration of cellulose differ from those resulting from the denitration of tri-nitrocellulose.

Whilst nitration with mixed nitric/sulphuric acids appears to be favoured for commercial working, many other processes have been described in the literature. The use of mixtures of nitric and phosphoric acids is stated by Bouchonnet¹⁵ and his co-workers to give products of high nitrogen content. Berl¹⁶ has claimed that in addition this process gives less micellar degradation than does nitration with sulphuric acid, and he also describes the influence of the acid concentrations on the degree of esterification. T. Tomonari¹⁷ has shown that the reaction mechanism of the nitration of ramie fibres with phosphoric acid/nitric acid/water mixtures corresponds with that for the conventional nitric/sulphuric acid/water mixtures. C. Trogus¹⁸ found that nitrocellulose of 7–13.9 per cent. nitrogen content may be prepared by the action of mixtures of concentrated nitric acid ($d. = 1.52$) and acetic acid, on fibrous cellulose in the absence of water: the presence of water reduces the nitrogen content. Products of higher nitrogen content may be obtained by the addition of phosphorus pentoxide or acetic anhydride to the nitrating mixture.

The use of a large excess of nitric acid may be avoided by nitrating in an indifferent organic solvent such as carbon tetrachloride according to Rogowin.¹⁹ An increased percentage of solvent lowers the degree of nitration and also the solubility of the product. Bouchonnet²⁰ states that mixtures of nitric acid and water with less than 35 per cent. of water nitrate cellulose, but cause hardening and considerable diminution of the final volume of the nitrocellulose. These drawbacks are overcome by the addition of alkali nitrates, sulphates, or phosphates to the mixture.

According to R. Dalmon²¹ the product obtained by nitration of cellulose by nitrogen pentoxide in carbon tetrachloride solution contains 14.2 per cent. nitrogen against 14.4 per cent. theoretical for the tri-nitrate, and the yield is 99.3 per cent. According to S. Rogowin²² additions of oxides of nitrogen (N_2O_3 , N_2O_5 , N_2O_4) to the nitric acid used in nitration produces an increase in the degree of nitration, the greatest being with N_2O_5 additions. The effect of pure nitrogen peroxide on linters and bleached sulphite pulp at 0° and 20° C. has been investigated by P. Schorygin.²³ He found that nitrogen peroxide does not nitrate cellulose but produces oxidation products soluble in alkali.

The physical properties of nitrocellulose can be varied widely according to the nature of the cellulose used and the method of nitration. Other things being equal, low viscosity esters, such as are

required for lacquers and dopes, are produced from low viscosity cottons, whilst the converse applies to the higher viscosity materials for explosives, films, and sheet plastics. The characteristic of nitrocellulose is its high inflammability, and for many plastic purposes this has been reduced by subjecting the product to a controlled partial de-nitration, or by adding fire-retarding agents to the plastic composition: among the latter are alkali halides, simple and complex phosphates, and urea.

Tomonari, Trogus, and Hess²⁴ found that nitrocellulose forms addition compounds with certain ketones which give definite Röntgen diagrams. A practical outcome of this is the formation of the nitrocellulose plastic celluloid. Camphor forms a definite addition product with nitrocellulose, and thus accounts for the fact that celluloid has remarkable weathering properties compared with those of other cellulosic plastics, in spite of the relative volatility of camphor compared with some of the other plasticizers used. Acetone is stated to form two definite compounds, one of which is a derivative of cellulose and the other of hydro-cellulose; this accounts for the difference in behaviour of nitrocellulose films in which acetone instead of ether/alcohol is used as the solvent. *m*-Xylene is also stated to form an addition compound with nitrocellulose, but this only in the presence of acetone.

(b) Miscellaneous Inorganic Esters.

Apart from the nitrate, few of the inorganic esters of cellulose appear to have attained any commercial importance, and of the derivatives described in the patent literature the phosphate and sulphate alone are of major interest. The production of both these was very logical since both these acids have been widely used, either separately or admixed, as catalysts in the production of cellulose acetate. Moreover, since it is well known that the use of phosphates, both inorganic and organic, in the preparation of cellulosic plastics and lacquers reduces the inflammability of these materials, it was logical to endeavour to produce an ester of low inflammability by introducing the phosphate radical into the cellulose molecule.

Champetier²⁵ found that if cotton linters are treated with solutions of H_3PO_4 containing 600 to 1,300 gm. per litre there is an increase in the amount of acid taken up to a maximum of 1,050 gm./l. An addition compound resulted after 15 hours which corresponded to the formula $3C_6H_{10}O_5H_3PO_4$. This compound was completely destroyed by washing with water, and the cellulose thus regenerated exhibited no trace of phosphate.

According to the I.G. Farbenindustrie A.-G.,²⁶ cellulose phosphate results when alkali cellulose from cotton linters is treated with an ice-cold solution of phosphorus oxychloride in benzene, the heat of reaction raising the benzene to the boiling-point. A tough magma settles to the bottom and is washed with alcohol and ether, vacuum-dried, and dissolved in water. The solution is freed from electrolytes

and the cellulose phosphate is precipitated by the addition of methanol.

Cellulose sulphates have attracted attention, although here again there is little evidence that these products have found commercial application. Caille²⁷ showed that cellulose sulphate is prepared by treating cotton with 15 times its weight of a mixture of equal parts of H_2SO_4 and glacial acetic acid at $45^\circ C.$ for 30 minutes, the fibre structure of the cotton being retained. Gebauer-Fulnegg, Stevens, and Dingler²⁸ treated cotton with chlorsulphonic acid at 100° in the presence of excess pyridine and obtained a gelatinous product which gave transparent colloidal solutions. Traube and his co-workers²⁹ found, however, that the prolonged action of chlorsulphonic acid on cellulose in the presence of pyridine does not lead to a homogeneous tri-sulphate.

(c) Cellulose Formate.

In spite of the fact that it has found very little industrial application, cellulose formate appears to have received more than its fair share of attention in recent times. By contrast with the other esters of organic acids the formylation of cellulose is effected with the acid itself, without the theoretical counterpart of acetic anhydride, but with the aid of a catalyst. Suitable catalysts are sulphuric acid, gaseous hydrochloric acid, zinc chloride, phosphorus pentachloride, &c.

(d) Cellulose Acetate.

It has been recorded that in the decade following the discovery of nitrocellulose over six hundred original contributions were published, but less than one-fourth that number appeared relating to cellulose acetate in the twenty years following its discovery. Once the possibilities of cellulose acetate had been appreciated, however, the tables were rapidly turned, and during the past quarter of a century there has certainly been no more fruitful field for research in the whole of cellulose plastics.

The industrial career of cellulose acetate has been a chequered one. Discovered by Schützenberger over seventy years ago, it received very little attention until 1894, when the first patent for its industrial preparation was granted to Cross and Bevan, but it was not until 1901 that it was produced on anything like a satisfactory scale. The early products were soluble only in the relatively costly and toxic solvents, such as chloroform and tetrachlorethane, so that the ester found limited commercial use until 1904–5, when Miles in America, and the Bayer Company in Germany, found that acetone-soluble cellulose acetate could be obtained by the mild acid saponification of the primary acetylation product. Following the development of this discovery, the manufacture of cellulose acetate assumed large proportions during the war years of 1914–18, when it was used on a large scale as a protective coating for aeroplane wings. At the

end of the war it was necessary to find an outlet for what was essentially a war material, and the huge plants which had been established for the production of cellulose acetate dope for aircraft were adapted to the more peaceful production of acetate rayon. While to-day rayon still claims the greater part of the world's output of cellulose acetate, this ester is being used in ever-increasing quantities in the production of films, foils, lacquers, protective coatings, and plastic masses. In view of its importance, the manufacture of acetone-soluble cellulose acetate will be described in greater detail.

The manufacture of cellulose acetate follows the normal process for the esterification of any alcohol, although, in order that the delicate structure of the cellulose may be preserved, some activating agent or catalyst is necessary. The industrial methods available fall, broadly, into two classes, the homogeneous and heterogeneous acetylation methods, although, as those who are familiar with patent literature will know, the number of possible variations of these general methods is, unfortunately, legion. The two general methods differ fundamentally in that the products of heterogeneous acetylation retain the original fibrous structure of the cellulose. Acetylation in homogeneous systems, in which the acetate passes into complete solution in the acetylating reagents as soon as it is formed, is almost universally adopted at the present time, although during the last few years the so-called non-solvent method has become increasingly popular, especially for the production of the higher acetates, where subsequent saponification or ripening is unnecessary. The same acetylating agents are usually used for both solvent and non-solvent methods of acetylation, namely, acetic acid and acetic anhydride, while sulphuric acid is still the most popular catalyst. The actual mechanism of the catalysis is not clearly understood, but it is assumed that there is the formation of intermediate products whereby the sulphuric acid unites, partly with the cellulose yielding cellulose sulphate, and partly with the acetic anhydride yielding acetyl sulphuric acid, $\text{CH}_3\text{CO}\cdot\text{O}\cdot\text{SO}_2\text{OH}$, which acts further as an acetylating agent, being finally converted into sulphoacetic acid, $\text{HOOC}\cdot\text{CH}_2\cdot\text{SO}_2\text{OH}$.

It will readily be understood that the uniform and even esterification of the somewhat complicated cellulose molecule is not a simple matter and, unless the lattice structure is opened up to permit the easy entry of the acetylating agent, heterogeneous products will result. Some form of pre-treatment of the cotton, either with organic and/or mineral acids, is now almost standard practice, since, not only is the product thus prepared more regular, but the ease of acetylation and hence the actual process time is favourably influenced. Apart from the pre-treatment, the acetylation takes place in two stages, the first resulting in the formation of the primary acetate, which may be converted without separation into the secondary product, the common acetate used in industry.

The following may be taken as typical of the present-day methods

for the acetylation of cellulose by the solution or homogeneous process. Air-dry cotton linters, with up to 8 per cent. water content, are dried at a low temperature (about 50°) to 2-3 per cent. moisture. It is inadvisable to use air-dry linters, since some of the relatively costly anhydride will be wasted in taking up the water present. On the other hand, the linters must not be too dry since they become horny and are consequently less reactive. The dry linters are pre-treated for several hours with glacial acetic with or without a small addition of a mineral acid, and are then transferred in batches of 150-200 lb., or in isolated instances several times these amounts, to a mixer of the well-known Werner-Pfleiderer type, into which the required quantity of an acetylating bath consisting of acetic acid, acetic anhydride, and sulphuric acid, pre-cooled to 0°, has been added.

For the safe control of the acetylation it is usual to record the reaction temperature graphically. When the cotton is first added there is a slight temperature rise, and the cotton absorbs the liquid. As the reaction proceeds with constant mixing, there is a slight fall in temperature with the brine 'on', and the reaction mass becomes definitely fluid or as usually stated 'sloppy'. The mass thereafter thickens and becomes quite pasty, this change being accompanied by a gradual rise in temperature. This corresponds with the actual acetylation period, and as it proceeds the mass becomes gradually stiffer and less opaque until it is finally transparent and light orange in colour. The reaction is allowed to continue with constant mixing and intermittent brine cooling, until a test sample examined under the microscope is entirely free from residual fibre. The product has now reached the primary stage, and acid hydrolysis is necessary to convert it into the secondary, acetone-soluble acetate.

When the primary acetylation is complete, water is gradually added in sufficient quantity to 'kill' the residual anhydride and to saponify the primary cellulose acetate, reducing the acetic acid content from, say, 59 to about 53-54 per cent. When the addition has been made the reaction mass is transferred into shallow copper vessels and maintained in a room at a uniform temperature of 20° for 50-72 hours, or until a test sample withdrawn from each pan shows that the saponification, or 'ripening' as it is called, has been carried far enough. The ripened product is separated from the golden-yellow syrup by the gradual and controlled addition of water, and the precipitated mass freed from dilute acid by centrifuging. The cellulose acetate is then washed free from acid, and finally stabilized by boiling for some time with very dilute mineral acid. The product is dried at moderate temperature. Since the size of the individual acetylation batches is more or less fixed by plant limitations, it is necessary to unite many batches to produce a homogeneous blend which is usually of the order of 5 or 10 tons. The user can thus be assured of absolute uniformity of product over a large bulk of raw material.

On these, the broad lines of current industrial production of

acetone-soluble cellulose acetate, many individual and combined improvements have been the subject of a vast number of patent specifications throughout the world, and reference can be made to but a few of these in this brief survey.

To open up the cellulose fibre and thereby facilitate the uniform penetration and action of the acetylation mixture numerous forms of pre-treatment have been suggested, although it would appear that treatment with the lower aliphatic acids with or without the addition of mineral acids is still the most favoured. G. A. Richter³⁰ recommends pre-treatment with sulphur dioxide gas followed by hydrogen peroxide, both in glacial acetic acid. The resulting sulphuric acid serves as a catalyst in the subsequent acetylation. The same worker has also recommended treatment with alkali followed by glycerol.³¹ Among numerous patented pre-treatment processes the following are of interest: propionic acid and keten;³² acetic acid and sulphuric acid;³³ phosphoric acid;³⁴ mixed halogen and acetic acid vapours.³⁵

For the solvent method of acetylation the diluent mainly used is glacial acetic. One of the most striking departures from this standard practice was the suggestion by the U.S. Industrial Alcohol Co.³⁶ to use liquid sulphur dioxide, a suggestion which was strikingly enough made almost simultaneously by the I.G.³⁷ This medium has the distinct advantage that when the acetylation is complete the sulphur dioxide is removed merely by releasing the pressure in the acetylation vessel, the cellulose acetate separating in light fluffy fibrous form. The use of liquid SO_2 also provides a valuable means of controlling the temperature throughout the reaction mass.³⁸ Other liquid solvent diluents which have been suggested to replace the standard acetic acid are monochloroacetic acid,³⁹ chlorinated aromatic hydrocarbons,⁴⁰ methylene chloride,⁴¹ and formaldehyde.⁴²

The number of catalysts recommended is legion, although here again commercial technique adheres to the early favourite sulphuric acid, itself the subject of many patents since the pioneer work of Lederer.⁴³ Other catalysts suggested include phosgene,⁴⁴ perchloric acid,⁴⁵ perchloric acid with mineral acids,⁴⁶ hydrofluoric acid,⁴⁷ benzene sulphonic acid.⁴⁸ The comparative action of the various catalysts has also received much attention and this work has been reviewed by Kruger,⁴⁹ and also by Trogus and Hess.⁵⁰

Saponification and purification of cellulose acetate has also received important consideration, but the purification, stabilization, and general after-treatment of the ester has been the focus of major attention in recent years. Stabilization calls for the removal of the unstable sulpho-esters of cellulose by mild acid saponification, usually by boiling the completely washed cellulose acetate with very dilute sulphuric acid.⁵¹ Other processes remove the deleterious sulpho-esters by solvent extraction in preference to their decomposition by chemical treatment. In like manner it is claimed that the stability of cellulose acetate is increased by treatment with aqueous oxalic acid,⁵² or by means of 0.136 per cent. of free chlorine

from sodium hypochlorite.⁵³ The increasingly stringent demands made by automatic injection has made this question of stability one of foremost importance in recent years, and in consequence of this concentrated research the quality of current commercial cellulose acetate has attained a remarkable degree of perfection.

The advancing demands of recent years have also influenced the technique of acetate manufacture in another direction, i.e. the production of high-clarity and water-white materials, suitable for the manufacture of clear sheet for aircraft screens and the like. Products of improved colour and colour stability have been obtained by fractional solution and also by fractional precipitation.⁵⁴ In some cases it has been found possible to separate the esters of lower clarity by making use of their granular size or physical nature by processes of sifting.⁵⁵ According to Martin,⁵⁶ products of excellent colour and clarity are obtained by passing an acetone solution of cellulose acetate through active carbon.

Fractional solution and precipitation has received more than mere academic interest in recent years, and both these methods have been shown to be efficient as a means of separating commercial acetone-soluble cellulose acetate into constituent fractions of widely differing colour, clarity, and viscosity.⁵⁷ With reference to viscosity G. R. Levi⁵⁸ has shown that grinding in a vibratory mill lowers the viscosity of the fractions, and such methods are recommended in preference to chemical treatment to reduce the viscosity of solutions of cellulose acetate. Among other publications dealing with fractionation of cellulose acetate, those of McNally and Godbout,⁵⁹ H. J. Rocha,⁶⁰ I. Sakurada,⁶¹ R. O. Herzog,⁶² and Clément and Rivière⁶³ are worthy of close attention.

(e) Cellulose Triacetate.

The position of triacetate in industry to-day is still, as it has always been, an anomalous one. At the beginning of the present century the cellulose acetate industry commenced with what was quite the logical process, namely, the production of a completely acetylated product. The difficulty in finding a suitable solvent led to the change-over which followed the discovery of Miles and gave birth to the cellulose acetate industry as we know it to-day. When the production of the acetone-soluble acetate had been developed to a high state of perfection attention was again turned to improving its water resistance, and quite naturally the position of the more water-resistant triacetate was again reviewed. Throughout the intervening years triacetate had not been entirely neglected, and especially during the past five years considerable progress has been made particularly in the production of fibrous triacetate. To-day cellulose triacetate appears to be at the cross roads. It is now produced in commercial quantities by both the solution and non-solution methods of acetylation, so that it is available as the rather hard and horn-like powder and also in fibre form resembling the original cotton.

At the outset it must be clearly understood that triacetate is a material quite as separate and distinct from cellulose acetate as is nitrocellulose. It must not be regarded merely as an improved form of cellulose acetate and consequently expected to conform to methods which have been developed for cellulose acetate. Just as cellulose acetate long suffered in plastics because it was worked and judged on the basis and standards of celluloid, so also triacetate is liable to suffer by reason of unfair comparison and competition with the acetone-soluble product. To emphasize the necessity for this distinction, triacetate is separately treated in this survey of cellulose derivatives used for plastics.

As has already been pointed out in describing the manufacture of cellulose acetate, in the commercial method now universally operated for the preparation of acetone-soluble material to-day the primary stage in the process yields the substantially fully esterified cellulose. The material can be separated at this stage by precipitation in the usual way, but the product is hard and horny, and difficult to stabilize and wash. For this reason considerable attention has of late years been devoted to the production of fibrous triacetate and its stabilization, and typical examples of the methods suggested are given in the patents of Otto Sindl,⁶⁴ E. Berl,⁶⁵ The Distillers Co. Ltd.,⁶⁶ and C. F. Boehringer.⁶⁷

Broadly the process is as follows. Cotton linters are pre-treated as in the standard acetylation process, and then treated with an acetylating mixture and an anti-solvent such as toluene,⁶⁸ benzene,⁶⁹ carbon tetrachloride,⁷⁰ or the like. The acetylation mixture usually contains acetic acid, acetic anhydride, and a catalyst such as concentrated sulphuric acid. The temperature of the acetylation is regulated at 25–40°, and the progress of the esterification is followed by examining the solubility of samples withdrawn at regular intervals. By contrast with the solvent process of acetylation there is little or no change in the outward appearance of the cotton right up to the point of complete esterification. When the test sample indicates a fully esterified product, the acetylating liquor is drained off, and the residue is expressed from the fibre as completely as possible. The combined sulphuric acid is next removed from the product, a step which may be regarded as the most vital in the whole process. A fibrous mass is not easy to treat, so that this difficulty is overcome by treating it with stabilizing agents admixed with alcohols or such like media which facilitate both the wetting of the fibre and the hydrolytic breakdown of the cellulose sulphoesters. A novel method of stabilization has been patented by Sindl⁷¹ in which instead of breaking down the unwanted esters by chemical treatment they are removed bodily by solvent extraction. This method has the advantage that no breakdown of the triacetate itself is possible, as may be the case where stabilization by boiling with dilute mineral acid is operated.

By one method or another the triacetate is thus freed from the unstable sulphur-containing products and is then freed from most

of the adhering liquid by centrifuging, and after being washed acid-free it is finally dried at a moderate temperature.

Cellulose triacetate thus prepared is obtained as a uniform white, fibrous material, very similar in appearance to the original cotton linters. It is usually less dense than normal linters, but slightly denser than the commercial acetone-soluble acetate. Having regard to its more complete acetylation one would expect triacetate to be a much more homogeneous and constant product than is the more common acetone-soluble variety. With an acetyl value of 61.0 to 61.8, the commercial triacetate approaches very near to the theoretical 62.5 required for three acetic acid radicals per C_6 unit. In triacetate, therefore, there are few unesterified groups, and careful and prolonged extraction of a good sample of triacetate has been unable to separate esters with acetyl value varying by more than 0.5. This contrasts with commercial acetone-soluble cellulose acetate, where the range of acetyl value of constituent fractions is frequently of the order of 50-60.

TABLE I. *Properties of cellulose triesters at 25° C.*

Ester	No. of carbon atoms	Density	Melting-point	Per cent. moisture regain		Contact angle vs. water	Work adhesion vs. water
				50% RH	100% RH		
(Cellulose) Acetate	0 2	1.618 1.377	.. Decomposes at 245	5.6 2.3	18.8 10.0	.. 50	.. 117
Propionate	3	1.268	239	1.3	4.4	78	87
Butyrate	4	1.178	183	0.7	3.5	84	79
Valerate	5	1.178	160	0.5	1.7	90	72
Caproate	6	1.110	87	0.3	0.9	93	68
Heptoate	7	1.081	97	0.2	0.8	100	59
Caprylate	8	1.058	85	0.1	0.9	99	61
Pelargonate	9	1.032	66	0.1	1.0	100	59
Caprate	10	1.026	64	0.3	1.5	100	59
Laurate	12	1.004	80	0.3	1.4	101	58
Myristate	14	0.991	87	..	1.5	104	55

Some interesting work on the cellulose triesters, from the acetate to the myristate, has been published by Sheppard and Newsome,⁷² and the data they have published are epitomized in Table I. Melting-points were determined by heating the sample in a glass capillary tube placed in a copper block, and densities were determined, using methyl alcohol as displacement liquid, since methyl alcohol wets the esters, especially the higher ones, much better than water, and gives a higher density value than water. The melting-points of the esters pass through a minimum at cellulose caproate, whereas the melting-points of the normal fatty acids themselves pass through a minimum at valeric acid: the influence of the cellulose residue is

thus noted. There is no definite evidence of an alteration of melting-point with odd and even numbers of carbon atoms as is noted with the free acids. The densities of the esters decrease regularly with increase in the number of carbon atoms, and in this case correspond to the behaviour of the free acid. The moisture regain apparently passes through a minimum near cellulose heptoate, although one would expect it to decrease with increase in the number of carbon atoms in the side chain. Quite definitely the cellulose character of the triester is progressively submerged as the length of the side chain is increased.

The higher acetates of cellulose belong to what is often referred to as the chloroform-soluble group, since they are soluble in chloroform and similar chlorinated hydrocarbons. The most outstanding solvent for triacetate is a mixture of methylene chloride and an alcohol, preferably methyl or ethyl, in proportion by volume of 90:10. Triacetate is also soluble in 90-100 per cent. formic acid, and frequently in glacial acetic acid. On the other hand, the higher esters are insoluble in acetone. There has been some speculation as to where acetone solubility ends and chloroform solubility commences, but this appears to vary between quite wide limits of acetic acid content, depending on the type of cellulose ester and its method of preparation. Generally speaking 55-56 per cent. acetic represents the upper limit of acetone solubility for commercial products produced by solvent acetylation, although acetone solubility has been observed in fibrous products having a much higher acetyl value. Yarsley⁷³ has produced an acetate containing 59 per cent. combined acetic acid which was soluble in acetone, but films prepared therefrom could not be redissolved in this solvent. Sakurada⁷⁴ states that chloroform solubility is dependent on the degree of acetylation and not on the starting material or conditions of preparation. He suggests that in the micelle the acetylation reaction progresses in molecular layers and the lattice forces (secondary valencies) of the non-acetylated portion hinder the solution of the acetylated part. By saponifying fibrous triacetate with HNO_3 or HClO_4 Sakurada has obtained partially saponified products containing 58.5 per cent. combined acetic acid which were entirely soluble in acetone and chloroform.⁷⁵

Generally speaking cellulose triacetate is less easily saponified than the secondary acetate, as one would expect from the lower percentage of hydroxyl groups in the micelle, so that triacetate products are, initially at any rate, more able to withstand the effect of dilute acid and alkali. Related to this, and possibly most important of all the physical characteristics of the triacetate, is its high resistance to moisture. Triacetate is very difficult to wet-out, and the dimensional changes brought about by continued contact with water, as also the loss of tensile strength when wet, are much less than is usually encountered with the acetone-soluble acetate.

Some interesting work on the action of water and water vapour on cellulose acetate films, with special reference to those products

formed from highly acetylated cellulose which approximate to the triacetate, has recently been published by Charriou and Valette. Some of the results obtained by these workers, showing the deformation of cellulose acetate films of various types, are collected in Table II. These workers regard the absorption of water by cellulose acetate compositions as a chemical combination of the hydrate type between water and the hydroxyl groups in the cellulosic composition. It is pointed out also that actual treatment with water is bound to remove a small amount of the plasticizing agent present in the film, and this action will be intensified by the subsequent drying.

From the results obtained, the conclusion is drawn that the production of cellulose acetate products of very low deformability is possible when esters containing of the order of 60 per cent. acetic acid are used. It is stated, furthermore, that, in view of the excellent properties of triacetate films, there appears to be no reason whatever why the dangerous nitro-cellulose should continue to be used.

TABLE II

<i>Acetic acid content of cellulose acetate used in the composi- tion % CH₃COOH</i>	<i>Nature of treatment of films</i>	<i>Deformation of films %</i>			
		<i>At end of 5 days</i>	<i>At end of 30 days</i>	<i>At end of 60 days</i>	<i>At end of 90 days</i>
52.3	Washing for 5 days	0.25	0.3	0.31	0.32
59.5	in running water at 20° C.	0.05	0.065	0.07	0.08
52.3	Washing for 8 days	0.1	0.1	0.1	..
59.5	in running water at 35° C.	0.06	0.07	0.08	..
52.3	Treatment for 30 min.	0.095	0.185
59.5	in water at 70–80° C.	0.025	0.04
55.9	Treatment for 30 min.	0.03	0.025	0.025	..
57.6	in boiling water	0.015	0.015	0.01	..
59.5		0	0	0	..

Apart from its increased water resistance, one of the most outstanding characteristics of cellulose triacetate is its superior electrical insulating properties. In the form of foils and their films, prepared by evaporation and by wet precipitation methods, triacetate films are now being widely used as insulating wrappings in place of the oil-impregnated paper and fabric hitherto employed. Some interesting comparative electrical data have been collected by Nowak, and these are given in Table III.

A review of the properties of plastics prepared from highly acetylated cellulose and a comparison of these with normal acetate-plastic and with aceto-butyrate plastic has been made by W. E. Gloor.⁷⁶ He found that a 58 per cent. acetic cellulose acetate gives a plastic which, whilst having all the properties of conventional acetate plastic, has much improved water- and heat-resistance. It gives inherently better gloss, shrinkage, and weather-resistance than standard acetate plastics, and can be formulated in the regular

ranges of flow, stiffness, and colour. The material produces plastics without critical moulding conditions and free of unusual odour.

TABLE III

<i>Material</i>	<i>Dielectric loss % on dried products</i>		<i>Dielectric constant on dried products</i>	
	<i>20° C.</i>	<i>75° C.</i>	<i>20° C.</i>	<i>75° C.</i>
Triacetate alone	0.9	0.7	3.0	2.8
Triacetate 20 per cent. phthalic acid ester	0.8	0.7	3.0	3.4
Triacetate 50 per cent. phthalic acid ester	0.8	1.6	3.8	4.2
Triacetate 20 per cent. mixed phthalates	0.9	1.2	3.5	3.7
Triacetate 20 per cent. tricresyl phosphate	1.2	1.5	3.5	3.8

MIXED ESTERS

Although a vast amount of work appears to have been done on the preparation of mixed esters of cellulose as is evidenced by the patent literature, few of these products have attained a commercial significance comparable with that of the acetate and nitrate. Most of the mixed esters appear to have been prepared for a specific purpose, usually to combine the outstanding properties of the simple esters. Typical examples of this are the nitro-acetates, aceto-butyrate, and propionates, which are among the few mixed esters which have attained commercial significance.

(a) Nitro-acetates.

From the viewpoint of rayon and plastics the major defect of nitro-cellulose was its inflammability. Early efforts to eradicate or minimize this having yielded but indifferent satisfaction, the work of finding a substitute was intensified and resulted ultimately in the production of cellulose acetate. This gave what was frequently referred to as 'non-inflammable celluloid', but the physical properties of the early products failed to equal those of celluloid. Attempts were thus made to effect the logical compromise and use a mixture of the nitrate and acetate, and later the mixed ester itself was produced in an endeavour to obtain a product which would give a safety cine film of the lowest possible degree of inflammability, but having tensile properties and water-resistance as nearly as possible equal to that of nitro-cellulose.

According to the patent literature a very considerable amount of research has been devoted to the production of nitro-acetates, but apart from limited application in the production of photographic films these mixed esters do not appear to have attained commercial importance. The reason is possibly to be found in the unduly increased production cost, and the fact that the products still retain

a certain degree of inflammability, yet are definitely inferior to nitro-cellulose in physical properties. The patented methods published fall broadly into three classes, (a) those based on the acetylation of cellulose nitrated to a low nitrogen content, (b) by the nitration of cellulose acetate, (c) by the simultaneous nitration and acetylation of cellulose. The preparation of nitro-acetates by these methods with reference to the patents involved has been reviewed by K. Roos,⁷⁷ who points out that the products of the various methods do not in general meet with the commercial requirements for low combustibility.

According to a British Celanese patent⁷⁸ mixed esters are prepared by the simultaneous application to cellulosic materials of organic esterifying agents and nitrating agents of such a strength that at least 3 per cent. of nitrogen, calculated on the esterified product, is introduced. The proportion of nitrogen may be much higher and examples are given varying from 10 to 13.79 per cent.; in the latter case the acetic acid content is 32.34 per cent.

(b) Mixed Esters of Organic Acids.

The mixed esters of organic acids have proved more fruitful fields for commercial development, and of these the major success appears to have attended the production and application of the aceto-butyrate. This is now available in commercial quantities in America and is sold under the names of Hercose C and Tenite II. The former according to Gloor⁷⁹ approximates to the triester and contains 2.2 acetyl and 0.8 butyric groups per C₆ unit.

The properties of some of the mixed esters have been summarized by Hagedorn and Möller⁸⁰ and are collected in the following table:

	<i>Strength in kg./sq. mm.</i>	<i>Extension %</i>
Aceto-propionate	9.7	12
Aceto-butyrate	7.3-8.5	20-25
Aceto-laurate	2.0-3.0	60-85
Butyro-laurate	3.5-5.0	60-70
Aceto-butyro-laurate	3.5	85
Aceto-benzoate	8.3	12
Butyro-benzoate	7.0	35
Naphthenate-laurate	1.2	200

The mixed esters are insoluble in water and alcohol, but soluble with varying ease in acetone, acetic acid, and chlorinated hydrocarbons. The lower members are insoluble or swell only slightly in benzene and its homologues, but the higher esters are soluble in these media.

(c) Cellulose Aceto-butyrate.

A large number of patents have dealt with the preparation of the aceto-butyrate. According to the Hercules Powder Co.⁸¹ cellulose

aceto-butyrate soluble in aromatic hydrocarbons is produced by pre-treating cellulose for 12 hours with 40–50 per cent. H_2SO_4 followed, after drying, with acetic acid for 15 hours, after which esterification is effected by treatment with butyric acid, acetic anhydride, and 0.5 per cent. H_2SO_4 at 35–50° C.

A general review of the properties of cellulose aceto-butyrate has been given by G. Schulze,⁸² whilst C. H. Penning⁸³ has reviewed the properties of this mixed ester with special reference to its application in the manufacture of moulded plastics.

Cellulose aceto-butyrate is a white flaky or granular material, similar to cellulose acetate in appearance. It is somewhat lighter than the acetate, the specific gravity being 1.21 for the mixed ester as against 1.31 for cellulose acetate. In the same way the plastics from these esters show variations, with the result that objects moulded from the aceto-butyrate weigh approximately 6 per cent. less than those from cellulose acetate. There are wide variations in the ratio of acetic to higher fatty acid content, but one commercial aceto-butyrate contains 18–22 per cent. butyrate calculated as butyric acid and 38–42 per cent. acetic acid calculated as acetic. Similarly, a commercial aceto-propionate contains 31 per cent. propionate and 15 per cent. acetate calculated as the respective acids. According to Fordyce and Meyer,⁸⁴ cellulose aceto-butyrate having 35–40 per cent. butyryl content is particularly suitable for the production of moulding compositions. The product is more compatible with highly water-resistant and non-volatile plasticizers than cellulose acetate, and in this way presents a wider choice of moulding composition. At the same time these plasticizers are retained much more permanently and in higher concentrations than those commonly used with cellulose acetate.

The moisture absorption of the aceto-butyrate is relatively low and plastics from this ester absorb only half as much water as do the corresponding plastics from cellulose acetate. Furthermore, the mixed ester requires less plasticizer than does the straight ester, and this adds to the improved resistance to distortion under varying conditions of temperature and humidity. These properties account for the superior weathering of the aceto-butyrate plastics which have been more than anything else responsible for the rapid advances made by these materials in the past two years.

According to Penning,⁸⁵ in moulding cellulose aceto-butyrate plastic flow increases uniformly with temperature up to a certain point, and beyond that the material flows considerably faster. This critical temperature varies according to the type of material and for Tenite II injection type H4 is 331.5° F. and for compression type S2 is 276° F. In consequence of this less pressure is required to mould the aceto-butyrate than is usual for the corresponding acetate plastic, and similarly it is possible to mould harder compositions in the aceto-butyrate with the production of moulded units having increased resistance to heat. In consequence also of the lower viscosity of the plastic after it reaches this critical temperature, injection

moulded units of cellulose aceto-butyrate have improved strength and show fewer flow lines in thick sections.

The outstanding properties claimed for the aceto-butyrate plastics compared with the normal cellulose acetate compositions are increased weathering resistance, low water absorption, unique flow characteristics, and compatibility with resins and plasticizers. Some remarkable weathering tests which were carried out with films of cellulose aceto-butyrate have been described by G. M. Kline.⁸⁶ The aceto-butyrate and aceto-propionate have accordingly been recommended in numerous patents for the production of photographic films, and particularly those which, like X-ray films, must lie perfectly flat. Another growing application of the mixed esters is in the production of clear lacquers for outdoor use where, up to the present, coatings having satisfactory resistance to weather and sunlight have not been available. A striking example of the utility of cellulose aceto-butyrate lacquers is as a coating for bronze statues, where the metal before coating is cleaned by treatment with trisodium phosphate.⁸⁷

(d) Miscellaneous Mixed Esters.

A wide range of mixed esters are described in the patent literature, but the majority of these appear likely to remain of little more than academic interest. Cellulose nitro-benzoate, containing 4.5 per cent. of combined benzoic acid, is prepared by treating nitro-cellulose with the aromatic acid chloride in the presence of an acid binding agent such as pyridine.⁸⁸ Cellulose aceto-benzoate results when cellulose is treated with the anhydrides of acetic and benzoic acids in the presence of a halogen catalyst.⁸⁹ Among the higher mixed esters which have been prepared by what is termed the 'higher ionization constant' method are cellulose aceto-salicylate which melts at 248–271° C. and is soluble in 75 per cent. solutions of alcohol-water and acetone-water, and cellulose aceto-metatoluate, m.p. 215–232° C. and soluble in 75 per cent. aqueous 1:4 dioxan.⁹⁰ Among other mixed esters which have been described and are worthy of mention are cellulose phenylaceto-laurate,⁹¹ aceto-crotonate,⁹² aceto-lactate,⁹³ aceto-phosphate,⁹⁴ aceto-butyro-naphthenate,⁹⁵ and aceto-phthalate,⁹⁶ the last reference gives a useful survey of the relevant literature.

THE CELLULOSE ETHERS

By comparison with the cellulose esters, which have passed their centenary, the ethers are of relatively recent date, the earliest work being recorded about 1905 and the first patents of Lilienfeld and also of Dreyfus in 1912. Since that time a large number of patents have appeared describing the commercial production of a wide variety of ethers, and their application in the production of lacquers, plastics, and coating compositions. In spite of their many attractive qualities the ethers have so far failed to justify early expectations

in the field of plastics, and such success as has been achieved has been limited to ethyl and benzyl cellulose. Methyl cellulose has also received considerable attention, but it finds little application in plastics.

(a) Methyl Cellulose.

Methyl cellulose was first described in 1912 in the original master patent of Lilienfeld,⁹⁷ and was prepared by treating cellulose with esters of inorganic acids, such as alkyl halides or sulphuric esters, in the presence of basic substances. Methyl cellulose is generally prepared by the action of methyl sulphate or chloride on soda cellulose. When methyl chloride is used the reaction is carried out in an autoclave on account of the low boiling-point.

Methyl cellulose is available commercially in two main varieties, one water-soluble, the other insoluble in water but soluble in alkali, the difference depending on the degree of substitution. One of the most interesting properties of the lower methyl celluloses is their solubility in cold water but insolubility in hot water.

(b) Ethyl Cellulose.

Many of the patents referring to methyl cellulose cover also the preparation of ethyl cellulose and vice versa, and the main points of interest are given in the publications of Lilienfeld⁹⁸ and of Dreyfus.⁹⁹ Triethyl cellulose was prepared by Hess and Müller,¹⁰⁰ by treating alkali cellulose with ethyl sulphate at 50–55°, seven treatments yielding an ethoxy content of 55.2 per cent. against the theoretical requirements of 54.8 per cent. Berl and Schupp¹⁰¹ have shown that, whereas methylation can be effected at 0°, ethylation with ethyl sulphate must be effected at 70–80°. Methods of preparation of ethyl cellulose using ethyl chloride have been reviewed by Nikitin,¹⁰² and also by Uschakov,¹⁰³ who found that best results were obtained by using 6 mols of ethyl chloride to 1 of cellulose, heating for 8–18 hours at 120–130°. The degree of ethylation increases as the water content decreases, but too highly ethylated compounds have undesirable properties. Increasing the amount of ethyl chloride used and decreasing the water content give lower viscosity in the final product. The preparation, properties, and some applications of ethyl cellulose have been reviewed by Trail¹⁰⁴ and also by Stark¹⁰⁵ and Koch,¹⁰⁶ the latter refers specially to products containing 47–48 per cent. ethoxy.

The effect of various reagents on the viscosity of ethyl cellulose solutions has been described by Ligrain,¹⁰⁷ who found that a fall in viscosity follows treatment with water at 120°, and that aqueous acids cause considerable fall in concentrations above 0.25 per cent. Alkalis have little effect, and metallic salts do not react in any specific manner but according to the pH. I. Sakurada¹⁰⁸ has investigated the dielectric properties of ethyl cellulose and found the molecular polarization particularly dependent on the concentration.

The possibilities of ethyl cellulose in the field of plastics have been reviewed by Wiggam¹⁰⁹ and also by Gibb,¹¹⁰ whilst Wiggam and Koch¹¹¹ stressed the advantages obtained by using mixtures of ethyl cellulose and resins. More recently Wiggam¹¹² has reviewed the latest advances made in the use of ethyl cellulose in extrusion coatings for wires and also in injection mouldings. Compression moulding requires approximately 275–325° F., and 2,000–4,000 lb. per sq. in. pressure, whilst both injection and extrusion moulding requires 325–425° F. Among the more novel applications of ethyl cellulose is its use in the grinding of pigments which has been described by Kautz.¹¹³

(c) Benzyl Cellulose.

By comparison with other cellulose derivatives benzyl cellulose is a development of relatively recent times since nothing was heard of it before the work of Gomberg and Buchler¹¹⁴ was published in 1920, but the benzyl chloride method is still the basis for the current commercial production of this ether. Since that time benzyl cellulose has attracted a considerable amount of attention, and in this country it can certainly be said that very rarely has a new chemical been launched on its industrial career with such publicity and high expectations as was given to benzyl cellulose nearly ten years ago.

Numerous as have been the patented processes which have been published for the production of benzyl cellulose, even more numerous have been those for its separation and purification. Unlike the cellulose esters, benzyl cellulose is obtained as an amorphous powder from which it is by no means easy to separate the etherifying agents. Most of the purification processes depend on the direct extraction of by-products from the crude ether as described in the I.G. Farbenindustrie's patent.¹¹⁵ In another patent¹¹⁶ the original gummy material is converted into a friable mass by treating it in a malaxating mill with a water-soluble salt such as common salt.

Benzyl cellulose resists alkali up to 20 per cent., is unattacked by sulphuric acid of accumulator strength, and has a high water resistance. It is thermoplastic and can be heated up to 180° C. without fear of decomposition, and being non-inflammable can be worked at high temperatures without danger. The possibilities of using benzyl cellulose in the production of plastics, insulating dopes, and films, and artificial leather products have been fully explored without much apparent success. According to Kalpers,¹¹⁷ solutions of benzyl cellulose are effective in the prevention of the rusting of metals. Meunier and Gonfard¹¹⁸ have reviewed the properties and methods of examination and analysis applied to benzyl cellulose.

THE SOLVATION AND PLASTICIZATION OF CELLULOSE DERIVATIVES

Since cellulose derivatives find little or no commercial application in the dry or raw state, but are always used in the form of a solution

or a thick dough or plastic, the question of their solvation and plasticization is one of first importance. Impetus was given to the production of nitrocellulose when suitable solvents were produced at an economic price. The fate of cellulose acetate may well have been sealed after the failures in the early years of the present century, had not the discovery of Miles in 1905 given a material soluble in the relatively cheap non-toxic acetone. By way of paradox interest once more centred round triacetate when the large-scale production of methylene chloride, which, admixed with alcohols, is an excellent solvent for the triester, became commercial. In like manner attention turned to the ethers, mixed esters, and ester ethers when it was found that these can frequently be dispersed in cheap hydrocarbon solvents.

Attempts have frequently been made to draw a hard-and-fast distinction between solvents and plasticizers. Whilst it can be said with general accuracy that all solvents are plasticizers, all so-called plasticizers are certainly not solvents. In German the distinction is more finely drawn between 'Gelatinier-mittel' and 'Weichmacher', the former have a definite dispersive action on the cellulose derivative, the latter are merely softeners, liquid fillers, or extenders. Many of the so-called plasticizers for cellulose acetate, for example, owe their action mainly to their ability to retain acetone, and the loose eutectic is the effective plasticizer. During recent years the development of plasticizers for cellulose derivatives has been a very fruitful field for chemical research, and there can certainly be very few stable high-boiling esters which at one time or another have not been described in the patent literature as a plasticizer for a cellulose derivative. Plasticizers for cellulose acetate have been particularly sought after; and mainly because the substances known and used on the commercial scale functioned less perfectly than does camphor with nitro-cellulose in the production of celluloid, they were earlier frequently referred to as camphor substitutes. Experience has shown, as it usually does, that it is rather the simple known materials which find ultimate favour in industry, so that, in spite of the vast number of new products recommended, industry clings to those used since pioneer days.

The solvent properties of nitrocellulose depend on its nitrogen content, the main solvents belonging to the homologous series of acetic esters (mainly ethyl, butyl, and amyl acetate), ketones, ether-alcohols, and binary mixtures of pure solvents with various alcohols. Methods of determining the strength of nitrocellulose solvents have been reviewed by Doolittle,¹¹⁹ whilst Durrans¹²⁰ has reviewed the methods used in the manufacture of the main cellulose ester solvents.

For cellulose acetate the main commercial solvent is acetone, although solutions of remarkable clarity are obtained in mixtures of methylene chloride and alcohol. These mixtures are indeed able to disperse esters approaching the triacetate which were early regarded as being soluble in only chloroform and tetrachlorethane.

The cellulose ethers and mixed esters are generally soluble in the

Solubility of ethyl cellulose and other cellulose derivatives

<i>Solvent</i>	<i>Cellulose acetate</i>	<i>Nitro-cellulose with 35% alcohol</i>	<i>Ethyl cellulose</i>	<i>Benzyl cellulose</i>
Methyl formate	S	S	S	S
Methylene chloride	SW-A	S	S	S
Ethyl formate	S	S	S	S
Dichlorethylene	I-A	I	S	S
Acetone	S	S	PS	PS
Ethyl acetate	SW	S	S	S
Chloroform	I	SW	S	S
Ether	I	SW	S	I
Ether-alcohol	I	S	S	SW
Petroleum ether	I	I	I	I
Carbon tetrachloride	I	I	S	SW
Methyl ethyl ketone	I	S	PS	S
Benzol	I	I	S	S
Ethylene dichloride	I-A	I	S	S
Isopropyl acetate	I	S	PS	PS
Trichlorethylene	I	I	S	S
Propyl alcohol	I	I	S	I
Propyl acetate	I	S	S	S
Dioxan	S	S	S	S
Toluene	I	I	S	PS
Butanol	I	I	S	I
Methyl cellosolve	S	S	S	PS
Butyl acetate	I	S	S	S
Ethylene chlorhydrin	S	S	S	S
Ethyl alcohol	I	I	S	I
Amyl alcohol	I	I	S	I
Cellosolve	I	S	S	S
Amyl acetate	I	I	S	S
Xylene	I	I	S	SW
Methyl cellosolve acetate	S	S	S	S
Cellosolve acetate	I	S	S	S
Cyclohexanone	PS	S	S	S
Ethyl lactate	S	S	S	PS
Pentachlorethane	I	I	S	S
Cyclohexanol	I	I	S	I
Diacetone alcohol	S	S	SW	PS
Methyl cyclohexanone	I	S	S	S
Cyclohexanol acetate	I	S	S	S
Butyl glycol	I	S	S	PS
Butyl lactate	I	S	S	PS
Benzyl alcohol	I	I	S	S
Benzyl acetate	I	S	S	S
Triacetin	S	S	I	I
Turpentine	I	S	I
Camphor-alcohol	S	I	S	I
Dipentene	I	I	S	SSW
Pine oil	I	I	S	PS
Glycol diacetate	S	S	PS	PS

S, Soluble. SW, Swollen. I, Insoluble. SW-A, Swollen but with addition of alcohol becomes soluble. PS, Partially soluble. SSW, Slightly swollen. I-A, Insoluble but with addition of alcohol becomes soluble.

cheaper and more common organic solvents, a fact which has stimulated interest in their commercial development. Glikman¹²¹ has shown that when benzyl cellulose is treated with alcoholic hydrochloric acid it becomes more soluble in benzene and these solutions are less viscous. According to Sakurada,¹²² non-polar solvents cannot dissolve benzyl cellulose completely, although they are usually good swelling agents. Kauppi and Bass¹²³ have described methods for the evaluation of solvents for ethyl cellulose and have shown that films of maximum tensile strength are obtained from alcohol/hydrocarbon solvents formulated in such a way that the solvent to evaporate last from the film consists almost entirely of hydrocarbon. A comparison of the solvent properties of the various commercial derivatives is given in the preceding table.¹²⁴

In the production of nitrocellulose plastics the plasticizer mainly used is the pioneer camphor. In nitrocellulose lacquers and dopes current favourites are again old favourites such as tricresyl phosphate and butyl phthalate. For cellulose acetate and the ethers the main plasticizers favoured are again those tried over many years such as the aryl and alkyl phosphates, alkyl phthalates, and triacetin.

A useful survey of plasticizers for cellulose acetate and aceto-butyrate has been made by C. R. Fordyce and L. W. A. Meyer,¹²⁵ which includes not only physical characteristics of most of the common commercial plasticizers but comparative data for cellulosic plastics containing them. They state that the maximum amount of a given plasticizer which may be successfully employed with cellulose acetate depends to some extent on the behaviour expected from the resulting composition. The values of maximum compatibility give no indication of retention during ageing.

The determination of the plasticizer content of a cellulosic plastic is frequently a matter of some importance. Ryan and Watkins¹²⁶ have recommended that the plastic material shall be cut into strips and distilled *in vacuo* on an oil bath at 250–260° C. Separation can be effected in a few hours and the accuracy is sufficient for all practical purposes. F. C. Thames¹²⁷ has described a method for the determination of phthalate plasticizers. The actual amount of plasticizer used will vary with the cellulose ester and with the purpose for which the cellulosic composition is destined to be used. In the case of plastics it will vary from 10 to 50 per cent. on the weight of cellulose derivative, and for dopes from 60 to 150 per cent. For a given result the cellulose esters usually require a higher plasticizer content than do the ethers.

Record of the development of plasticizers for cellulose derivatives has occupied a prominent part in technical and patent literature in recent years, and general reviews of the position from time to time have been published by Yarsley,¹²⁸ Kraus,¹²⁹ Metzinger,¹³⁰ and Münzinger.¹³¹ During the past three years, however, less attention appears to have been paid to the development of new plasticizers and more concentrated work has been applied to the improved production of known and tried materials. Among the newer cellulose

acetate plasticizers which have attained some popularity are the sulphamide derivatives and glycollates, which have been fully described by Carswell.¹³²

Among the necessary properties of a satisfactory plasticizer Münzinger¹³³ gives first place to low volatility. Accordingly the determination of volatility of plasticizers has received much attention, although Wolff and Rabinowicz¹³⁴ have shown that the volatility of a plasticizer when heated in air is not necessarily a measure of the rate at which the substance will be eliminated from a film or plastic. L. Ivanovszky¹³⁵ has devised an apparatus for the automatic determination of the volatility of plasticizers. The effect of plasticizer addition on the volatility and solvent balance of hydrocarbon mixtures has been studied by J. B. Dorsch.¹³⁶

THE MANUFACTURE OF PLASTICS FROM CELLULOSE DERIVATIVES

(a) Sheets, Rods, and Tubes.

Sheets of cellulosic plastic are most widely produced by what has come to be known as the 'celluloid technique', a process which was developed originally for the production of sheet celluloid. The cellulose derivative is mixed with a suitable solvent and plasticizer in a mixer of the Werner-Pfleiderer type and is then filtered through high-pressure filters. The filtered plastic is transferred to heated malaxating rolls, where it is continuously sheeted out to render the mass homogeneous and to remove excess volatile solvent. Some idea of the nature of the plastic hide on the rolls is given in Fig. 4. When the required consistency has been attained the hides are stacked in regular manner and trimmed to standard size. They are next subjected to heat and pressure for some hours in a hydraulic press where the separate layers are pressed into a solid block about 6 in. thick which is in the same operation firmly anchored to a substantial metal bed plate: this plate fits on the moving table of the slicing machine. This table moving forward encounters an inclined knife which removes a surface-layer varying in thickness according to the knife setting. The knife advances automatically between each cut, which is repeated until the whole of the plastic has been sliced down to the bed plate. The manner in which the cut sheet rolls from the block in front of the inclined cutting knife is shown in Fig. 5. The sheets are then stoved at constant temperature to remove excess of volatile solvent, the time required depending on their thickness.

The sheets produced in this way display the lines of the cutting knife, so that it is necessary to polish them or apply any other desired embossing. This is effected in a multi-platten steam-heated press, each sheet of cut plastic being placed between two plates of highly polished nickel. The highly polished sheets, both of metal and cellulosic plastic, have to be handled with great care, as can be seen from Fig. 6.

Where decorative material, or material conforming to any special



FIG. 4. Rolling Celluloid 'Dough' prior to formation of block.
(By courtesy of B.X. Plastics, Ltd.)

configuration is required, this is effected by admixing diversely coloured plastic or pressing together variously coloured sheets in a regular geometric pattern. The packing, cutting, and repacking of the plastic has frequently to be repeated many times until the desired configuration is attained. A detailed description of the production of transparent and decorative cellulose ester plastic sheet has been given by Bonwitt.¹³⁷

An alternative method for the production of thick sheet has been



FIG. 5. Slicing Celluloid Sheet from block.
(By courtesy of B.X. Plastics, Ltd.)

described in the patents of the Fiberloid Co. Here the dough-like plastic is forced through a long flat orifice, and the sheet thus formed is subjected to longitudinal and transverse tension. It is claimed that in this way the tensile strength of the sheet is increased owing to regular orientation of the micelles under the tension applied.



FIG. 6. Polishing Transparent Celluloid and Cellulose Acetate Sheet.
(By courtesy of B.X. Plastics, Ltd.)

This process is somewhat similar to the standard method applied in the production of rods and tubes. Here the plastic prepared as for sheet manufacture is reduced to granular form and is introduced into the hopper of the extruding machine. Heat and pressure are applied, and the plastic material evolves from the nozzle as a rod

or tube accordingly. By the use of coloured plastic multicoloured material can be produced conforming to any desired configuration.

An alternative method of producing tubes by the spiral winding of sheet plastic has been described in patents of the Celluloid Corp. Tubes produced in this way are recommended for barrels for fountain pens, and have the advantage that, since a particular configuration can be more accurately reproduced in sheet than in extruded tube, the use of sheet may offer advantages in certain cases.

(b) Films and Foils.

The distinction between sheet and film is a perfectly arbitrary one. Material produced by the so-called casting process is usually regarded as film, whilst that cut from a block is regarded as sheet. Sheet plastic is thus available in standard size of 24 in. \times 54 in., and in thickness from 10 mils upwards. Cast film most usually covers the range up to 10 mils, although commercial film produced in this manner is available up to 15 mils. Cast film is usually produced at widths of 21 or 42 in.; in some instances even wider.

The commercial methods for the production of film and foils fall into two classes, (a) the dry or evaporative processes, and (b) the wet or precipitation methods. The latter are applied in the production of viscose foils for wrapping purposes, but these are beyond the scope of present consideration. The production of triacetate foils by precipitating fatty acid solutions of this ester in aqueous baths has been described in patent literature.

The commercial plant available for the production of films and foils by the evaporative process falls into two classes according as the film-forming solution is cast on the surface of an endless metal band or on that of a rigid wheel or drum. The bands are usually of copper and are 14 or 28 metres long and up to 50 in. wide: more recently endless nickel bands have been produced which by contrast with the copper can be burnished to give a mirror finish. Thus, whereas copper bands require to be coated with a layer of material, such as a gelatine solution, to give a glass-like casting surface, the polished nickel bands require no such preparation. In like manner the surface of the casting wheel is frequently burnished or plated and thus requires no preparation beyond periodic polishing. Since in many cases mild steel wheels are used, a gelatine or similar casting surface has to be prepared. The preparation of this 'mirror-finish' layer of gelatine on an extensive band or wheel is, as may be imagined, an operation requiring extreme care and skill.

In the case of band machines the band passes round two metal cylinders about 1 metre diameter and slightly wider than the band, and for the greater part of its travel is enclosed in a vapour-tight casing containing heating elements. In the actual casting of the film the cellulose ester solution, after very careful filtration and de-aeration, is poured or cast on to the gelatine or nickel surface from a V-shaped hopper or spreader, which is located above one of

the supporting drums in the case of a band machine, or a little below top centre in the case of a wheel or drum. A uniform layer of the solution is thus applied to the polished casting surface which moves forward into the heated enclosed space where the solvent gradually evaporates, leaving the solid film. The speed at which a revolution of the band or wheel is completed will depend on the thickness of the film to be cast, as naturally a thick layer will take much longer before all the volatile solvent has been removed and a rigid and handleable film is obtained. At the end of the complete revolution the film is sufficiently 'dry' to remove it from the casting surface and to pass it round rollers into a heated cabinet attached to the casting machine, usually styled the after-drying cabinet. Here the last traces of volatile solvent are removed from the film, which is finally reeled in rolls of 500 or 1,000 ft. ready for use. The whole process, from the preparation of the casting solution down to the removal of the finished trimmed film, requires costly apparatus and the constant application of skilful care which can only come of long experience. A detailed description of the outstanding plant required has been given by Bonwitt.¹³⁸

In this manner are produced films and foils of cellulose acetate, nitro-cellulose, and ethyl cellulose: the latter are used for certain insulating purposes and for the tipping of cigarettes. Cellulose acetate films are now quite widely used for electrical insulation and in 9 mils thickness for X-ray photographic film base; 10 mil cast acetate film has been recently used in large quantities in the production of windows for civilian gas-masks. Celluloid film is still the major demand for photographic purposes, decorative work, colour cards, and many general utility purposes. With the exception of the substandard 16 mm. and 9 mm. film the bulk of the many millions of feet of cine film used throughout the world to-day is still celluloid, and 3½ mil celluloid is the base for amateur roll film.¹³⁹

(c) Moulding and Manipulation of Cellulosic Plastics.

During the past few years the manipulation of cellulose plastic sheet, notably celluloid and cellulose acetate, has grown into a considerable industry. The working of celluloid into washable collars, table-tennis balls, battery boxes, baby toilet goods, and the like is, of course, an old industry, but it is only in recent years that the manipulation of cellulose acetate sheet has assumed importance. This side of the industry grew out of the manufacture of letters for advertisement signs in the well-known pillar-box red, and then came the production of components for aircraft. To-day windscreens and covers for gun turrets, landing lights, wheel spats, strut fairings, ammunition chutes, and many other units are fabricated from transparent or filled acetate sheet. This branch of the industry is capable of considerable expansion and already it has extended to the production of display models, from motor-car bodies to gas heaters, which show at once the outward form and the internal working

parts of the commercial unit. In the hands of a skilled workman remarkably intricate shapes can be prepared from cellulose acetate plastic sheet by the application of the required heat and local pressure.

Thin sheet and foil is also now widely used in the fabrication of

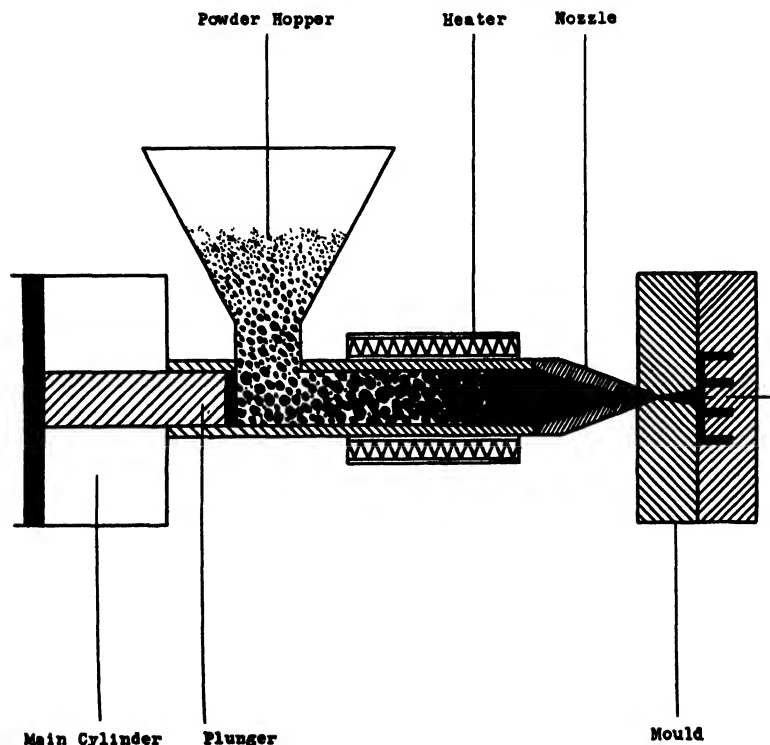
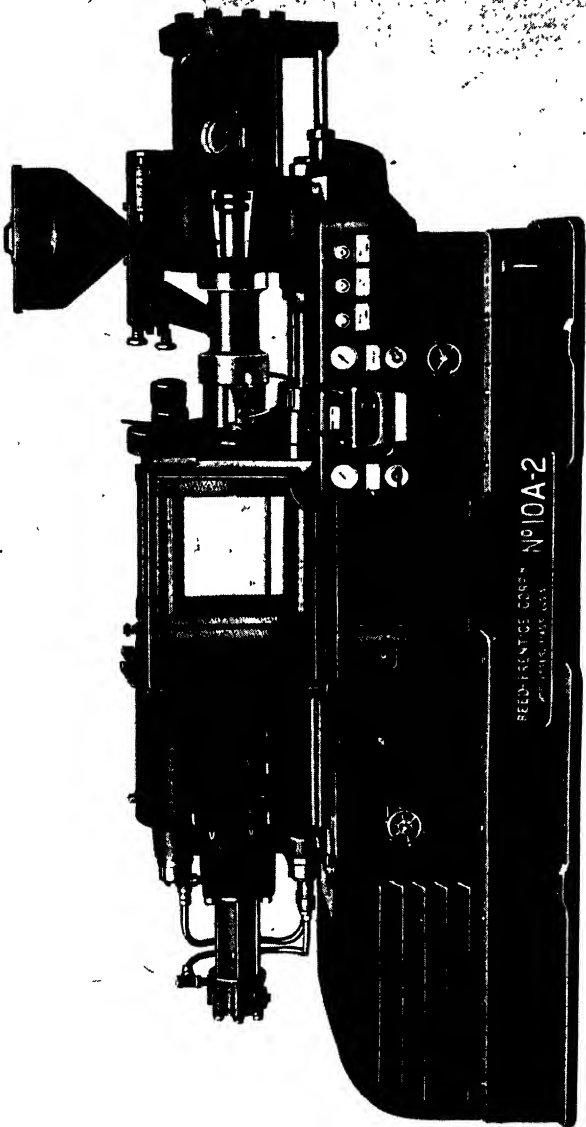


FIG. 7. The Injection Moulding Process.

containers for decorative and utility purposes. Containers for the display of food and cosmetics, and as selling containers for sponges and many soft goods, are now fabricated from transparent or decorative cellulose acetate sheet.

It is in the field of actual and direct moulding, however, that acetate plastic finds its major application. Two methods of moulding are available, one the conventional compression, or hot and cold moulding, the other the so-called injection moulding process. In both of these the acetate plastic is used in fine granulated form, although the actual nature of the composition used depends on the method of moulding to be applied. The compression moulding process is a simple one in which the powder is introduced into a mould which is cored for steam and water. The mould is filled with the



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FIG. 8. Fully Automatic Injection Moulding Machine.
(By courtesy of Alfred Herbert, Ltd., Coventry)

required charge of powder, is heated, and closed by pressure, after which it is cooled and the moulded unit extracted. Owing to the relatively fluid nature of the acetate plastic when hot, relatively low moulding temperatures and pressures may be used, and this also permits the use of moulds of light construction.

In the past few years the compression moulding of acetate plastic

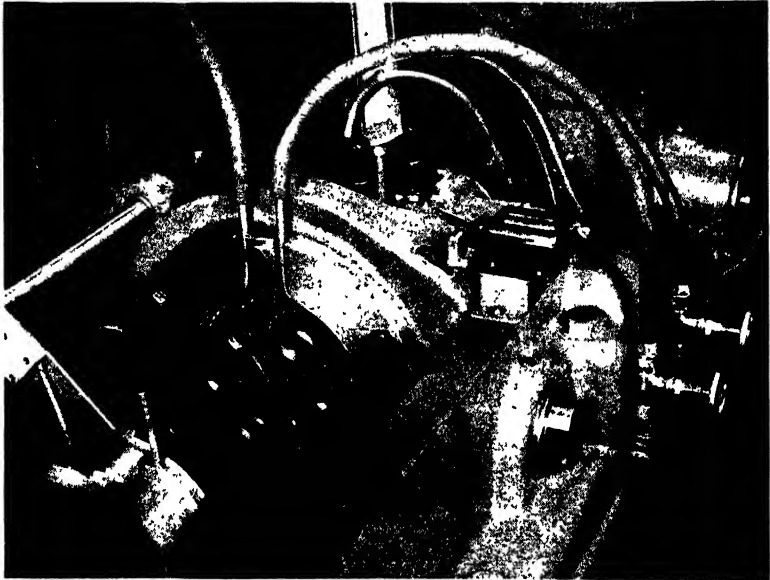


FIG. 9. Injection Moulding, showing multiple mould for buttons.
(By courtesy of B.X. Plastics, Ltd.)

has faded into insignificance in view of the phenomenal advances which have been made by the injection process, which is considered by some to be one of the major developments of this plastic age. There has been some dispute as to the actual inventor of the injection moulding of cellulose acetate, but the Eichengruen patents, which lapsed in this country some years ago, must receive this credit.¹⁴⁰ In the injection process the plastic is rendered fluid by the application of heat and in this condition is forced under high pressure into the cold or slightly warm mould. Under these conditions the plastic is shot into the mould at high velocity.¹⁴¹ Machines for injection moulding may be hand, hydraulic, or power operated. Whereas the early hand machines were limited to the production of moulded units of but a few grammes in weight, the latest multi-shot fully automatic machines can produce units weighing several hundred grammes. Some idea of the efficiency of the process can be obtained from the brief specification of a modern automatic injection machine

which reads: Machine for units up to 6 oz. in weight—300/400 shots per hour, maximum pressure on material 20,000 lb. per sq. in.; capacity 30 sq. in. at maximum pressure. The weight of this machine is given as 12,000 lb.

In this country cellulose acetate is still the premier injection plastic and the increasingly stringent demands of modern automatic machines have had much to do with improvements in the quality, particularly heat stability, of commercial cellulose acetate. To maintain colour stability at 160–200° in an acetate plastic would have been deemed an impossibility but a few years ago. The general working of the injection process is shown diagrammatically in Fig. 7, whilst Figs. 8 and 9 illustrate a modern automatic injection machine and give a close-up view of the mould when open after the ejection of the moulded unit.

REFERENCES

1. I. Miura, *J. Cellulose Inst. Tokyo*, 1938, **14**, 453 B; 1939, **15**, 167 B.
2. S. Hermanowicz, *Przemysł Chem.*, 1939, **23**, 93
3. U. Ponnillo, *Ind. Eng. Chem.*, 1939, **31**, 657; see also B P 480,170, 480,252, 489,302.
4. B. T. Ardashov, *Ind. Eng. Chem.*, 1933, **25**, 575–81.
5. W. D. Munson, *ibid.*, 1930, **22**, 467–71.
6. A. J. Hall, *Cellulose*, 1930, **1**, 176 8, 194.
7. Wanda K. Farr, *J. Applied Physics*, 1937, **8**, 228–32.
8. *Kolloid Z.*, 1926, **39**, 98
9. G. L. Clark, *Ind. Eng. Chem.*, 1930, **22**, 478
10. W. N. Haworth, *Chemistry and Industry*, 1939, **58**, 923.
11. Lunge and Bebic, *Z. angew. Chem.*, 1901, **14**, 486.
12. F. L. Nathan, *J.S.C.I.*, 1909, **28**, 177–87.
13. E. P. Partridge, *Ind. Eng. Chem.*, 1929, **21**, 1044–7.
14. T. Tomonari, *J.S.C.I., Japan*, 1935, **38**, 58 B–69 B
15. A. Bouchonnet, F. Trombe, and Mile G. Petitpas, *Bull. Soc. Chim.*, 1937 (v), **4**, 560–70.
16. E. Berl and G. Rueff, *Cellulosechemie*, 1931, **12**, 53–62; also B.P. 470,292.
17. T. Tomonari, *Cellulosechemie*, 1936, **17**, 29–34.
18. C. Trogus, *Ber.*, 1931, **64**, 405–7.
19. I. Rogowin and P. Pazadina, *Cellulosechemie*, 1934, **15**, 32 4.
20. A. Bouchonnet, *ibid.* 894–904.
21. R. Dalmon, *Compt. rend.*, 1935, **201**, 664 5; also 1123 4.
22. S. Rogowin and A. Tichonow, *Cellulosechemie*, 1935, **16**, 11–12
23. P. P. Schorygin and E. V. Khaiz, *J. Gen. Chem. (U.S.S.R.)*, 1937, **7**, 188–92.
24. Tomonari, Trogus, and K. Hess, *Z. physikal. Chem.*, 1932, **B. 16**, 241 and 351.
25. G. Champetier, *Compt. rend.*, 1933, **196**, 930.
26. I. G. Farbenindustrie, B.P. 279,796.
27. A. Caille, *Chim. et Ind.*, 1925, **13**, 11; 1926, **15**, 189.
28. E. Gebauer-Fulnegg, O. Dingler, and W. H. Stevens, *Ber.*, 1928, **61**, B 2000.
29. W. Traube, B. Blaser, and E. Lindemann, *Ber.*, 1932, **65**, 603
30. G. A. Richter (Brown Co.), U.S.P. 2,006,977.
31. G. A. Richter, U.S.P. 2,064,384; B., 1938, 1142.
32. E. I. Du Pont de Nemours, B.P. 436,885; B., 1936, 11.
33. H. Dreyfus, B.P. 325,231; Kodak Ltd., B.P. 345,800; I.G. Farbenindustrie, B.P. 281,927; B.P. 356,073; B., 1930, 414; B., 1931, 533; B., 1931, 1006.
34. Eastman Kodak, U.S.P. 1,823,359.
35. Ruth-Aldo Co., Inc., B.P. 303,134; U.S.P. 1,668,483; B., 1929, 892.
36. U.S. Industrial Alcohol Co., B.P. 306,531; B.P. 329,718; B., 1930, 708.
37. I.G. Farbenindustrie, B.P. 301,036; B.P. 343,655; B.P. 355,144; B., 1931, 968
38. U.S. Industrial Alcohol Co., B.P. 355,382; C. F. Boehringer u. Soehne Ges., B.P. 312,242; B., 1931, 1005.
39. I.G. Farbenindustrie, B.P. 305,674; see also B.P. 203,599, B., 1930, 814.
40. Soc. Scottish Dyes, Ltd., F.P. 608,028.
41. R. Hoffmann, F.P. 697,156.
42. Heberlein & Co., B.P. 312,280; see also B.P. 383,043; B., 1933, 57.
43. L. Lederer, B.P. 11,749/1900.
44. E. I. Du Pont de Nemours, B.P. 421,599; B., 1935, 266.
45. C. F. Boehringer, G.P. 602,318, 600,979.
46. Eastman Kodak Co., U.S.P. 2,005,398; B., 1936, 907.
47. Soc. Anon. Italiana d. la Soc. d. Chatillon, Ital. P. 267,550; see also Soc. Usines de Rhône Poulenc, F.P. 754,961.
48. Chem. Works formerly Sandoz, B.P. 489,928; B., 1939, 167.
49. D. Kruger and W. Roman, *Z. angew. Chem.*, 1934, **47**, 58–60 and 806–10.
50. C. Trogus and K. Hess, *ibid.*, 1934, **47**, 30–2.

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51. Eastman Kodak Co., U.S.P. 2,101,984; see also Celanese Corp. America, U.S.P. 2,095,334.
52. Celanese Corp. America, U.S.P. 2,105,570.
53. Celanese Corp. America, U.S.P. 2,109,496.
54. C. Dreyfus, F.P. 689,134.
55. Celanese Corp. America, U.S.P. 1,933,720
56. Celanese Corp. America, U.S.P. 2,050,381; cf also G. R. Levi and A. Giera, *Gazz. Chim. Ital.*, 1937, 67, 719-23.
57. See F. Ohl, *Kunstseide*, 1930, 12, 468-72; 1932, 14, 3-7.
58. G. R. Levi, U. Villotta, and M. Monticelli, *Gazz. Chim. Ital.*, 1938, 68, 589-92.
59. J. G. McNally and A. P. Godbout, *J. Amer. Chem. Soc.*, 1929, 51, 3095-101.
60. H. J. Rocha, *Kolloid chem. Beihfte*, 1930, 30, 230-48.
61. I. Sakurada and M. Taniguchi, *J.S.C.I., Japan*, 1932, 35, 249-53 B.
62. E. O. Herzog and A. Demopasko, *Cellulosechemie*, 1932, 13, 25-31.
63. L. Clément and C. Rivière, *Bull. Soc. Chim.*, 1934 (5), 1, 1075-82.
64. O. Sindl, B.P. 411,260; B.P. 414,461; B.P. 488,707; F.P. 755,981-2; U.S.P. 2,066,584; D.R.P. 578,212; B., 1934, 714; B., 1934, 923.
65. E. Berl, B.P. 381,991; B.P. 415,329; B.P. 405,825; U.S.P. 2,039,290; Can P. 344,804.
66. The Distillers Co Ltd, B.P. 437,907; B.P. 451,660; B., 1935, 95; B., 1936, 1087.
67. C. F. Boehringer und Soehne Ges., B.P. 363,700; B.P. 387,533; B.P. 396,657; B.P. 413,368; B.P. 424,419; D.R.P. 600,979 82; D.L.P. 641,126; D.L.P. 643,863; B., 1932, 236; B., 1933, 301; B., 1933, 860; B., 1934, 829; B., 1935, 400.
68. Eastman Kodak Co., U.S.P. 2,036,382.
69. E. Berl, B.P. 381,991.
70. L. Lederer, G.P. 200,916; H. Dreyfus, B.P. 325,224.
71. O. Sindl, B.P. 411,260; U.S.P. 2,066,584, F.P. 755,981; D.R.P. 578,212; see also Afag Finanzierungs A.-G., B.P. 488,707, Swiss P. 173,730
72. S. E. Sheppard and P. T. Newson, *J. Phys. Chem.*, 1935, 39, 143-52.
73. V. E. Yarsley, *Über die Herstellung und physikalischen Eigenschaften der Cellulose-Acetate*, Springer, 1927.
74. I. Sakurada and T. Morita, *J.S.C.I., Japan*, 1938, Supp. binding, 381-2.
75. I. Sakurada, loc. cit., 385-6.
76. W. E. Gloor, *Mod. Plastics*, 1940, 17 (April), 62-3
77. K. Roos, *Synth. Appl. Finishes*, 1935, 6, 94-7, 114-16.
78. British Celanese, B.P. 341,147; B., 1931, 343; see also E. Berl, B.P. 483,474; B., 1938, 1400; and U.S.P. 2,125,880.
79. W. E. Gloor, *Paint, Oil and Chem. Rev.*, 1937, 99, No. 10, 30, 32, 34.
80. M. Hagedorn and P. Moller, *Cellulosechemie*, 1931, 12, 29.
81. Hercules Powder Co., U.S.P. 1,973,693; B., 1935, 720.
82. G. Schulze, *Farben Chem.*, 1937, 8, 78-80.
83. C. H. Penning, *Modern Plastics*, 1939, Oct., 38-9.
84. C. R. Fordyce and L. W. A. Meyer, *Ind. Eng. Chem.*, 1940, 32, 1057.
85. C. H. Penning, loc. cit.
86. G. M. Kline, *Symposium on Plastics*, 1937.
87. C. Maters, *Official Digest*, 1939, 190, 393.
88. G.P. 411,268.
89. F.P. 435,507; see also H. Dreyfus, B.P. 403,645, 403,646; B., 1934, 191.
90. U.S.P. 1,785,466; see also U.S.P. 1,861,200.
91. I.G. Farbenindustrie, B.P. 305,947, add. to B.P. 283,181 and B.P. 297,766.
92. Kodak Ltd., B.P. 287,880; B.P. 289,853; Soc. Usines de Rhône, B.P. 331,260
93. Eastman Kodak, U.S.P. 2,000,596; B., 1936, 690; B.P. 338,201; B., 1931, 242
94. I.G. Farbenindustrie, B.P. 270,347; Eastman Kodak, U.S.P. 2,008,986; B., 1936, 1146.
95. I.G. Farbenindustrie, B.P. 338,798; B., 1931, 108.
96. C. J. Malm and C. R. Fordyce, *Ind. Eng. Chem.*, 1940, 32, 405-8.
97. L. Lillienfeld, B.P. 12,854/1912.
98. L. Lillienfeld, B.P. 14,320, 156,735, 163,016, 181,391-5; B., 1924, 51; B.P. 203,346-7; B., 1924, 11; 177,809-10; B., 1924, 11; 200,815-16, 200,827, 200,834.
99. H. Dreyfus, B.P. 176,420, 187,639, 269,531.
100. K. Hess and A. Müller, *Ann.*, 1927, 455, 209.
101. E. Berl and H. Schupp, *Cellulosechemie*, 1929, 10, 41.
102. N. I. Naktin and J. I. Rudneva, *J. Appl. Chem. (U.S.S.R.)*, 1933, 6, 45-9
103. S. N. Uschakov, *Plast. Massy*, 1931, 6, 17-26.
104. D. Trall, *J.S.C.I.*, 1934, 53, 337 T-342 T.
105. C. Stark, *Kunststoffe*, 1932, 22, 107-10.
106. W. Koch, *Ind. Eng. Chem.*, 1937, 29, 687-90.
107. N. Ligrain, *Rev. gen. Mat. plast.*, 1937, 13, 123-9.
108. I. Sakurada and S. Lee, *Kolloid Z.*, 1935, 72, 320-5.
109. D. K. Wiggam, *Mod. Plastics*, 1936, 14 (No. 2), 31.
110. D. A. Gibb, *Mod. Plastics*, 1937, 15 (No. 2), 23.
111. D. R. Wiggam and W. Koch, *Mod. Plastics*, 1938, 16 (No. 2), 28.
112. D. R. Wiggam, *Mod. Plastics*, 1939, 17 (No. 2), 48-50.
113. H. Kautz, *Farbe u. Lack*, 1939, 233-4.
114. M. Gomberg and C. Buchler, *J. Amer. Chem. Soc.*, 1920, 42, 2060, 43, 1914
115. I.G. Farbenindustrie, B.P. 403,982; B., 1934, 234.
116. I.G. Farbenindustrie, B.P. 265,491.
117. H. Kalpers, *Wasser u. Abwasser*, 1938, 36, 40.
118. L. Meunier and M. Gonfard, *Compt. rend.*, 1932, 194, 1839-42.
119. A. K. Doolittle, *Ind. Eng. Chem.*, 1938, 30, 189-203.
120. T. H. Durrans, *Chem. and Ind.*, 1935, 585-92.
121. S. A. Ghikman, *Plast. Massy*, 1937, 2, 3-30.
122. I. Sakurada, *J.S.C.I., Japan*, 1933, 36, 656 B-659 B; see also K. Atsuki, *J.S.C.I., Japan*, 1934, 37, 615 B-619 B.
123. T. A. Kauppl and S. L. Bass, *Ind. Eng. Chem.*, 1938, 30, 74-9.

124. Hercules Powder Co., *Ethyl Cellulose*, p. 5.
125. C. R. Fordyce and L. W. A. Meyer, *Ind. Eng. Chem.*, 1940, **32**, 1053-60.
126. J. D. Ryan and G. B. Watkins, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 191-2.
127. F. C. Thames, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 418.
128. V. E. Yarsley, *Synth. and Appl. Finishes*, 1936, **6**, 239-41, 280-1; see also *Brit. Plastics*, 1932, **4**, 246-7, 266, 324.
129. A. Kraus, *Farbe u. Lack*, 1937, pp. 509, 521, 533.
130. E. F. Metzinger, *Paint, Oil and Chem. Rev.*, 1938, **100**, No. 10, 6-9, 36-7.
131. W. Münzinger, *Kunststoffe*, 1934, **24**, 97-101, 137-43, 164-7, 222-31, 260-5, 310-15.
132. T. S. Carswell, *Ind. Eng. Chem.*, 1920, **21**, 1176-8; see also *Plast. Prods*, 1933, **9**, 361-2.
133. W. Münzinger, loc. cit.
134. H. Wolff and J. Rabinowicz, *Farben Ztg*, 1932, **37**, 585.
135. L. Ivanovszky, *Farbe u. Lack*, 1932, 244.
136. J. B. Dorsch, *Ind. Eng. Chem.*, 1940, **32**, 279-81.
137. G. Bonwitt, *Das Celluloid*, Berlin, 1933.
138. G. Bonwitt, *Das Celluloid*, Berlin, 1933, 445-55.
139. See also *Ind. Chemist*, 1930, **2**, 73.
140. Cf. H. Staullinger, *Brit. Plastics*, 1932, **4**, 520-2.
141. See R. Jones, *Brit. Plast. Year Book*, 1932, 57-67; also A. Amigo, *British Plastics*, 1937, **9**, 552 and 579.

CHAPTER III PHENOL-FORMALDEHYDE RESINS

By C. A. REDFARN

I

INTRODUCTION, RAW MATERIALS, RESIN PRODUCTION, AND THEORY OF REACTION

THE most important thermo-setting plastics are those derived from the resins obtained from phenols and formaldehyde. That phenols and aldehydes would react to give resinous products was recorded by Baeyer in 1872, but to the classical organic chemist of that time the synthesis of a resinous mass, which could not be purified by crystallization, was regarded with suspicion; it is not therefore very surprising that there were no developments of Baeyer's discovery.

It has also been recorded that in 1893 G. T. Morgan prepared an amber-coloured resin from phenol and formaldehyde, but again on this second emergence of phenolic resins the time was not ripe for their industrial development.

In the first decade of this century, when phenol and formaldehyde had ceased to be mere chemical reagents and were becoming available in industrial quantities, L. H. Baekeland, a U.S. citizen of Belgian origin, put on the market his phenol-formaldehyde products known as Bakelite.

Raw Materials.

The phenols used in the production of phenol-formaldehyde resins are ordinary phenol, particular grades of cresylic acid (i.e. grades consisting of mixtures of the three isomers *meta*-, *para*-, and *ortho*-cresol, each present in specified amounts) and, to a less extent, 1:3:5-xyleneol, and resorcinol. Certain *para*-substituted phenols (e.g. *p*-*tertiary* butyl phenol) are used for the production of oil-soluble resins for use in paints and varnishes.

Phenol, cresols, and 1:3:5-xyleneol are derived from coal-tar, which is the chief source of phenols for synthetic resin production. Synthetic phenol (see p. 106) has become available within the last few years, and recently it has been stated¹ that phenols derived from petroleum are a potential source of raw material for plastics.

Production of phenols from coal-tar. Wood is composed chiefly of cellulose and lignin (about 25 per cent.); lignin is a complex substance of aromatic structure. The geological processes involved in the conversion of wood into coal result in the elimination of the cellulose component and the conversion of the lignin into a bituminous mass known as coal. If the conversion process proceeds farther, anthracite, which consists chiefly of carbon with very little hydrogen, is produced.

When bituminous coal is distilled the chief products obtained are coal gas (consisting chiefly of methane and hydrogen), ammonia, coal-tar, and a residue of coke (consisting chiefly of carbon).

The distillation is carried out in coke ovens, vertical retorts, and horizontal retorts, and the composition of the coal-tar varies according to the method used. Most of the coal-tar used for the production of phenols is obtained from horizontal retorts.

Coal-tar is submitted to fractional distillation and the following fractions are collected:

- (1) *First runnings*, B.R. 45–105°, containing ammonia, carbon disulphide, and furfuran.
- (2) *Light oil*, B.R. 105–210°, consisting chiefly of benzene, toluene, and xylene, and also containing basic substances such as aniline and piperidine.
- (3) *Carbolic oil*, B.R. 210–40°, consisting chiefly of phenol and naphthalene with small amounts of cresols and xylenols.
- (4) *Creosote oil*, B.R. 240–70°, consisting chiefly of cresols and xylenols with some heavy hydrocarbons.
- (5) *Anthracene oil*, distilling about 270°, consisting chiefly of anthracene and homologues.
- (6) *Residue* of coal-tar pitch.

The carbolic and creosote oils are for all practical purposes the only sources of phenols for synthetic resins used in this country. In their crude state the phenols (phenol, cresols, xylenols, ethyl phenols, &c.) are known as tar acids. Phenol when purified is called in the trade 'carbolic acid', and mixtures of the three cresol isomers, usually containing xylenols, are called 'cresylic acid'.

The distillates containing tar acids are washed with caustic soda solution (23° Tw.) in tanks fitted with agitators, and the liquor run into settling tanks in which the layer containing the sodium salts of the tar acids sinks to the bottom. This layer is removed and treated with carbon dioxide under pressure, allowed to settle, and the regenerated tar acids, free from hydrocarbons, are then run off. It may be necessary to add some concentrated sulphuric acid to the tar-acid-salt liquor, as the carbon dioxide does not decompose all of the sodium salts; at the same time the sulphuric acid materially reduces the amount of residual water.

The aqueous layer containing sodium carbonate and/or bicarbonate may be 'causticized' by treatment with lime, and caustic soda recovered.

The tar-acid layer obtained by treatment of the carbolic oil is distilled and then redistilled to give fairly pure phenol.

The tar-acid layer obtained from the creosote oil is fractionally distilled and various 'cuts' taken according to the grade of cresylic acid and xylenols required.

Phenol, C_6H_5OH , is obtained in the form of large colourless crystals which melt when absolutely pure at 42.5° and boil at 181.7°. The grade used in synthetic resin work has a melting range of

41.5–42°, the lowering of the melting-point being due to the presence of a trace of cresols.

On exposure to air, particularly in the presence of traces of metals, phenol turns pink, a colour change which is believed to be associated with the formation of quinoid bodies. This tendency to colour change is exhibited to some extent in all of the synthetic resin products derived from phenol.

Phenol, although it has a hydroxyl group, has more of the properties of an acid, since the hydrogen atom in the hydroxyl group is appreciably ionized. Phenol is strongly corrosive, and if allowed to remain in contact with the skin can cause burns which do not heal readily.

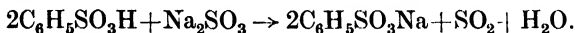
Synthetic phenol.² Several processes were developed during the 1914–18 war for the production of phenol from benzene, but that depending on the sulphonation of benzene as its first step seems to be the one most favoured. Under normal conditions synthetic phenol was not manufactured to any great extent in this country, the process, or rather the existence of the plant and its potential use, being used as a price stabilizer of coal-tar phenol.

Considerable variation in detail is possible in the benzene sulphonation process, but the broad outlines of the variation found to be most successful seem to be as follows:

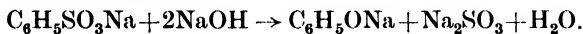
- (1) Benzene is sulphonated with sulphuric acid:



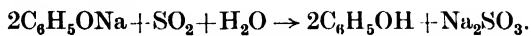
- (2) The sulphonate is treated with sodium sulphite to give the sodium salt:



- (3) Sodium benzene sulphonate is fused with caustic soda to give sodium phenate:



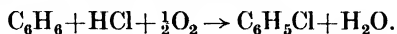
- (4) Phenol is liberated from sodium phenate solution by means of sulphur dioxide:



Phenol is extracted from the resultant liquor with tricresyl phosphate, washed with dilute sodium carbonate to remove traces of sulphur dioxide and purified by distillation.

It has recently been announced that the Durez Co., U.S.A.,³ are making synthetic phenol by the Raschig process, in which a vapour mixture of benzene, hydrochloric acid and air is passed through a catalyst to give a mixture of chlorbenzenes, from which monochlorobenzene is removed by distillation. Next a vapour mixture of monochlorobenzene and steam is passed through a catalyst to give phenol and hydrochloric acid. A continuous process is worked.

The first stage is exothermic. It is carried out at 230° and proceeds according to the following equation:



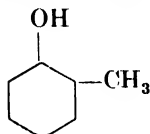
About one-tenth of the benzene is converted at each pass, so that the reactant stream contains benzene, monochlorobenzene, polychlorobenzenes, carbon monoxide, carbon dioxide, and water.

The second stage is endothermic and carried out at 425°; it can be represented by the following equation:

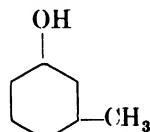


The by-products obtained besides hydrochloric acid and water are oxydiphenyl and diphenyl ether.

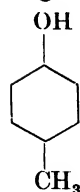
Cresol, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, has three isomeric forms which, when obtained together, are known as cresylic acid.



Ortho-cresol is, when pure, a white crystalline solid f.p. 31°, b.p. 191°: the freezing-point is not necessarily equal to the melting-point.



Meta-cresol is a liquid, f.p. 12°, b.p. 205.5°.



Para-cresol is, when pure, a white crystalline solid of m.p. 36°, b.p. 202°.

In order to obtain a satisfactory thermo-setting resin from a phenol and formaldehyde it is believed that the two *ortho*- and the *para*-positions should be available for reaction.

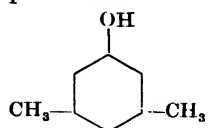
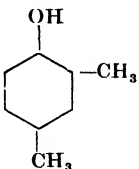
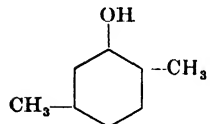
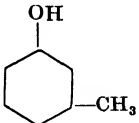
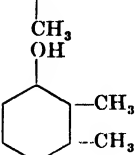
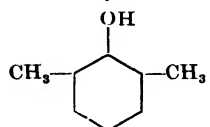
Only the *meta*-isomer can fulfil these conditions, but the isolation of pure *meta*-cresol is not an economic operation, since it would have to compete with phenol.

Ortho- and *para*-cresol will give with formaldehyde resins which will thermoset, although rather slowly, in spite of the fact that this does not conform with the concepts of functionality, as generally applied to the reactivity of phenols (cf. Chap. XV).

In consequence it is the commercial practice to prepare for synthetic resin work grades of cresylic acid with a high *meta*- and low *ortho*-content. In particular the grade covered by B.S.S. No. 521, 1933, calling for 50-5 per cent. *meta*-cresol, and not more than 5 per cent. *ortho*-cresol, with the balance chiefly *para*-cresol with a little xylenol, is in normal times largely used for the production of a

slightly cheaper grade of phenolic moulding powder. Another grade containing only 40 per cent. of *meta*-cresol is also used, as it has been found that even this low *meta*-content will give a thermo-hardening resin.

Xylenol or dimethyl phenol, $(\text{CH}_3)_2 \cdot \text{C}_6\text{H}_3 \cdot \text{OH}$, has six isomers possible:

	<p>1:3:5-xylenol <i>meta</i>-5-xylenol 1:3-dimethyl-5-hydroxybenzene</p>	<p><i>m.p.</i> <i>b.p.</i> 66° 221.5°</p>
	<p>1:2:4-xylenol <i>meta</i>-4-xylenol 1:3-dimethyl-4-hydroxybenzene</p>	<p>25° 211°</p>
	<p>1:2:5-xylenol <i>para</i>-xylenol 1:4-dimethyl-2-hydroxybenzene</p>	<p>75° 211.5°</p>
	<p>1:3:4-xylenol <i>ortho</i>-4-xylenol 1:2-dimethyl-4-hydroxybenzene</p>	<p>65° 222°</p>
	<p>1:2:3-xylenol <i>ortho</i>-3-xylenol 1:2-dimethyl-3-hydroxybenzene</p>	<p>73° 213°</p>
	<p>1:2:6-xylenol <i>meta</i>-2-xylenol 1:3-dimethyl-2-hydroxybenzene.</p>	<p>49° 202°</p>

The xylenols are obtained as high-boiling fractions in the distillation of the tar acids obtained from carbofic and creosote oil. The first four are certainly present and there are probably small amounts of the other two. In view of the closeness of the b.p. of the xylenols it is difficult to separate them by fractional distillation, so that xylene is generally sold according to the 'cut', i.e. a distillate boiling between two specific temperatures; however pure 1:3:5-xylene can be obtained commercially. It will be noticed that only 1:3:5-xylene has the two *ortho*- and *para*-positions free, so that this isomer or close 'cuts' consisting largely of this isomer are the

only ones really suitable for the production of thermo-setting resins. Xylenol formaldehyde resins have a limited use in plastics manufacture, one outlet being in the production of thermo-setting resins used in the production of brake and clutch linings.

Formaldehyde. Formaldehyde, CH_2O , is a gas which liquefies at -21° and solidifies at -92° . It is prepared by the catalytic oxidation of methanol (synthetic methyl alcohol) at about 450° .



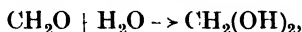
By this means formaldehyde is obtained as a solution in water and methyl alcohol containing about 40 per cent. CH_2O by volume (i.e. 40 gm. CH_2O per 100 c.c. of liquid) or 37 per cent. by weight (i.e. 37 gm. CH_2O per 100 gm. of liquid), and is known as 'formalin'. Aqueous solutions of formaldehyde tend to deposit a white precipitate of formaldehyde polymers; this tendency is to a large extent overcome if methyl alcohol is present, so commercial formalin usually contains 7-11 per cent. methyl alcohol.

On standing, formalin becomes slightly acid by reason of the following reaction:



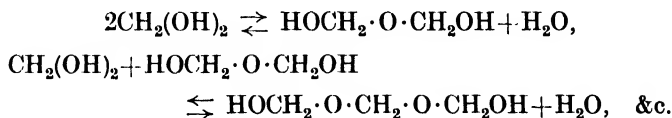
The percentage of formic acid usually present is about 0.2-0.3 per cent.

It is now generally recognized that formalin contains little CH_2O as such, but rather methylene glycol,⁴



and its polymeric hydrates.

According to Walker,⁵ the following products are in equilibrium in formalin:



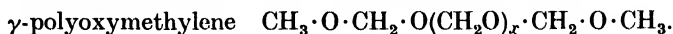
According to Homer, the order of polymerization of the poly-methylene glycols is from 6 to 50.⁶

Formaldehyde falls in with the general observation that the first member of a homologous series of compounds usually has distinctly different properties from the rest of the series. In fact formaldehyde is unique in the aldehyde series in that formaldehyde is the only aldehyde to give rapidly thermo-setting resins with, for example, phenol and urea, and that it is so far the only aldehyde which will 'formolize' casein.

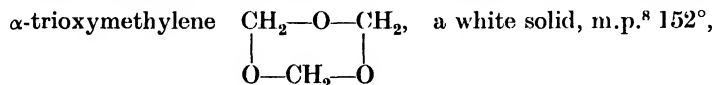
Paraform. Paraform, a solid polymerized variety of formaldehyde, is a white powder of indefinite melting-point, about 160° . It is obtained commercially by evaporating formalin in the presence of a small amount of acid. Its composition varies considerably with

the mode of preparation. It consists of from 95 to 97 per cent. of complex polymers $(\text{CH}_2\text{O})_n$ and its hydrated form $(\text{CH}_2\text{O})_n \cdot \text{H}_2\text{O}$, in which $n = 20$ to 100 ,⁷ the balance being loosely combined water.

The compounds present in paraform are mainly:

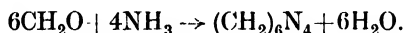


α -polyoxymethylene is very unstable and is decomposed by alkalis, whilst the γ -modification is more stable and resistant to alkalis, the difference in behaviour being ascribed to the difference in *end* groups.

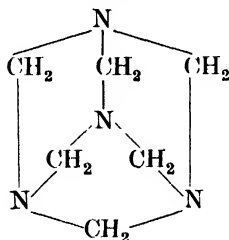


is present only in traces in commercial paraform. It is obtained by the action of a trace of sulphuric acid on hot formaldehyde vapour. The polymerization of formaldehyde and of ethylene oxides is further discussed in Chapter XVI.

Hexamethylene tetramine (hexamine or hexa), $(\text{CH}_2)_6\text{N}_4$, a white solid, is formed as its name implies, by the combination of six molecular proportions of formaldehyde with four molecular proportions of ammonia.

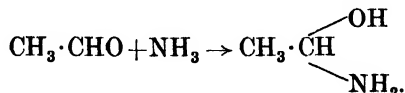


When 0.880 ammonia is added to formalin a violently exothermic reaction takes place to give hexamethylene tetramine. Hence care should be exercised in synthetic resin work when mixing these two liquids. The structural formula generally ascribed to it is:



When heated, hexamethylene tetramine decomposes and does not show a proper melting-point.

It might be noted that the reaction between ammonia and formaldehyde, the first member of the homologous series of aliphatic aldehydes, is different from that of the rest of the series of which the reaction with acetaldehyde to give acetaldehyde ammonia is typical:



Hexamethylene tetramine is used as a hardening agent for phenolic resin, and, as will be shown later, it acts both as a basic catalyst and a formaldehyde donor.

Production of Phenol-formaldehyde Resins.

The original resins made by Baekeland, were made from phenol and formaldehyde with an alkaline catalyst, preferably ammonia or caustic soda. This process is now known as the one-stage process.

A typical method of making an ammonia-catalysed resin consists of boiling under reflux a mixture of phenol and formalin in the molecular ratios of 1:1.5 with about 5-15 per cent. of 0.880 ammonia on the phenol content. The boiling is continued until the condensation products cloud out to give a liquor which readily separates into two phases on standing, the resinous phase being on top and the aqueous phase underneath. The liquor is submitted to vacuum distillation at about 90°, with or without first separating the aqueous layer. On distillation the resinous layer becomes thicker and eventually reaches a stage at which it will set to a brittle yellow resin on cooling. If the distillation is prolonged, or too high a temperature used, the resin will suddenly turn into a gel full of vapour pockets. Further heating transforms the gel into a hard infusible mass. Such a resin is therefore described as *thermo-setting*. When the distillation has proceeded far enough to give a syrup which will set readily on cooling, the liquor is run out of the reaction vessel into a shallow tray and allowed to cool.

The following nomenclature is used to describe the various stages through which the resin passes:⁹

Bakelite A, A stage resin, or resin A. A resin made on a 1:5 phenol-formaldehyde ratio with an alkaline catalyst, taken to the condition in which it is liquid when hot and solid when cold. The resin is soluble in alcohol, acetone, and aqueous alkalis.

Bakelite B, On heating, Bakelite A is carried forward to a condition in which it merely softens but does not melt on heating; it will swell in solvents, but will not dissolve.

Bakelite C, or C stage resin. Further heating gives a hard infusible insoluble resin which represents the final stage of resinification.

Another system of nomenclature for the same type of resin, used largely on the Continent, is as follows:

Resol or **Resole**: liquid soluble resin.

Resitol or **Resitole**: solid, soluble, fusible resin (cf. Bakelite A).

Resit or **Resite**: infusible, insoluble resin (cf. Bakelite C).

Bakelite A is the type of resin used in the original moulding powders. It was dissolved in methylated spirit and mixed with wood-flour, lime, and colouring bodies. The dough obtained was dried, powdered, and used for hot moulding, the lime present acting as an accelerator. In a later variation of this process the mixing

was carried out on hot rollers, without methylated spirit. This process, known as the one-stage process (because the phenol, formaldehyde, and ammonia are reacted together in one operation), is of historical interest only, practically all of the modern phenolic moulding powder being made by the two-stage process.

Resin A, however, is still used in the production of laminated materials and, particularly if made with caustic soda as catalyst, for spirit-soluble stoving lacquers.

Two-stage process. By far the greatest use of phenol-formaldehyde resins is in moulding powders. Phenolic moulding powders made by the one-stage process suffer from certain disadvantages. Since one-stage resin is thermo-setting, all through the distillation stage of its production the resin is advancing steadily towards the B stage, and the difficulty arises of getting rid of the remnants of the water still present before the resin becomes too thick; moreover, the residual phenol is difficult to distil off. As shown on pp. 113-16, it will be appreciated that the thermo-hardening of A-stage resin is associated with the change of methylol groups ($-\text{CH}_2\text{OH}$) attached to a phenol nucleus into methylene bridges ($-\text{CH}_2-$) joining two phenol nuclei together. Such a reaction involves the liberation of water molecules which must inevitably remain in the final heat-cured resin composition. The presence of ionized bodies such as water and free phenol in a moulded phenolic composition has a decidedly adverse effect on the electrical properties. Since the bulk of phenolic mouldings are used as electric insulators, the presence of water and free phenol in the material is an obvious disadvantage.

In the *one-stage* process the ammonia added as catalyst is largely 'used up' in the preliminary reaction, so that it has only a very slow catalytic effect on the final conversion to the C stage. Lime is added to catalyse the final conversion, and whilst rapid-curing moulding powders can be made by this expedient, the process is difficult to control and the presence of added lime raises the mineral content of the finished mouldings. For general electric and utility purposes a high mineral content is a disadvantage in a moulding.

These defects of the *one-stage* process are substantially overcome by the employment of the *two-stage* process.

The resin used in this process is known as 'Novolak', and it is made by reacting 1 molecular proportion of phenol with less than 1 molecular proportion of formaldehyde in the presence of an acid catalyst.¹⁰ The formaldehyde ratio usually favoured is about 0.8 of a molecular proportion: recently Megson¹¹ has from experimental work given academic reasons why this ratio is to be preferred.

If strong mineral acids (hydrochloric and sulphuric) are used as catalyst the amount required is about 0.1 to 0.3 per cent. on the phenol content. Mineral acids are apt to give a violent reaction, so oxalic acid (1.0-3.0 per cent. on the phenol) is commonly employed, since it gives a more even, but slower, reaction.

The reaction mixture of phenol, insufficient formalin, and acid catalyst is boiled under reflux until the condensation product will settle out readily in the hot, if the liquor is allowed to stand. The next step is vacuum distillation to give eventually a syrup, which on cooling sets to a colourless brittle resin known as 'Novolak'. If cresylic acid (e.g. the grade covered by B.S.S. No. 521/33) is used as the phenol, the product is known as 'Cresol-Novolak'.

Novolak resins, since they are made with insufficient formaldehyde, are not theoretically capable of forming cross-linked bodies by methylene bridges, i.e. they are substantially *non-thermo-setting*. Further, since they are made with acid catalysts they contain few methylol groups¹² and so are not capable of liberating any quantity of water on further reaction.

It follows that in the production of Novolak resin an intensive vacuum distillation—without much danger of gelling in the reaction vessel—can be carried out with the object of freeing the resin from water, uncombined phenol, and volatile low mol. wt. condensation products.

In order to thermo-harden a Novolak resin, heating with more formaldehyde, preferably with a basic catalyst, is required. By adding 10 to 15 per cent. of the Novolak weight of hexamethylene tetramine to the resin the requisite amount of formaldehyde is obtained, and at the same time the basic catalyst in the form of combined ammonia is added. On heating the mixture a *C-stage* resin very similar to that obtained by the one-stage process is produced. An important point from the electrical insulator aspect is that the conversion of Novolak to Bakelite C is an anhydrous reaction. Novolak itself is substantially free from methylol groups, so little water can be produced from that source, and hexamethylene tetramine does not contain elements of water.

The ammonia in Bakelite C, whether made by the one-stage process or via Novolak, is substantially in a 'bound' condition. Little research work concerning the nature of this 'bound' condition seems to have been carried out.

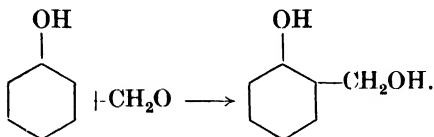
Theory of Reaction between Phenol and Formaldehyde.

The two *ortho*-positions and the *para*-position of phenol are particularly reactive towards formaldehyde, and it is probable that the *ortho*-positions are rather more reactive than the *para*-position. In the production of phenol-formaldehyde moulding resins and spirit-soluble resins for stoving lacquers the phenol-formaldehyde ratio ultimately arrived at is generally about 1:1.5, a ratio which is required for the two *ortho*-positions and the *para*-position to be completely reacted with formaldehyde.

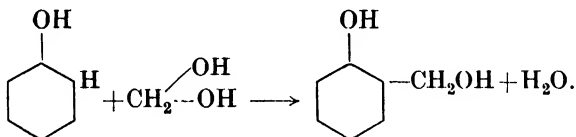
On functionality considerations (cf. Kienle's postulates, Chapter XV) phenol has a reactivity of 3, and formaldehyde, reacting as methylene glycol, a reactivity of 2, giving a 3:2 system which should be capable of thermo-setting. *Meta*-cresol, 1:3:5-xyleneol, and resor-

cinol, each having three reactive positions, give with formaldehyde thermo-setting resins, whilst *ortho*- and *para*-cresol, with only two reactive positions, give 2:2 systems with formaldehyde and hence non-hardening resins, conclusions which *in the main* are borne out by practical experience. In the writer's opinion, however, this is not the whole story, since there appear to be other possibilities of reaction besides the two *ortho*- and *para*-positions where phenols and formaldehyde are concerned. Also there are certain practical aspects of the behaviour of resins from formaldehyde and various phenols which do not entirely fit in with the classical conceptions of functionality. The matter is full of interesting possibilities, and is worthy of systematic investigation (cf. Chapter XVI).

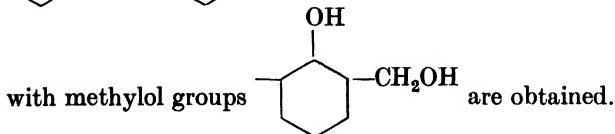
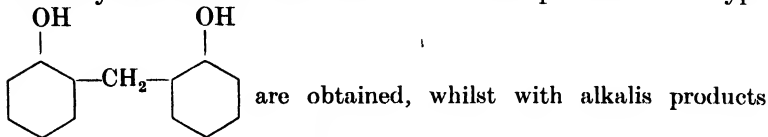
The first stage of the reaction between phenol and formaldehyde is the formation of saligenin, hydroxy-benzyl alcohol:



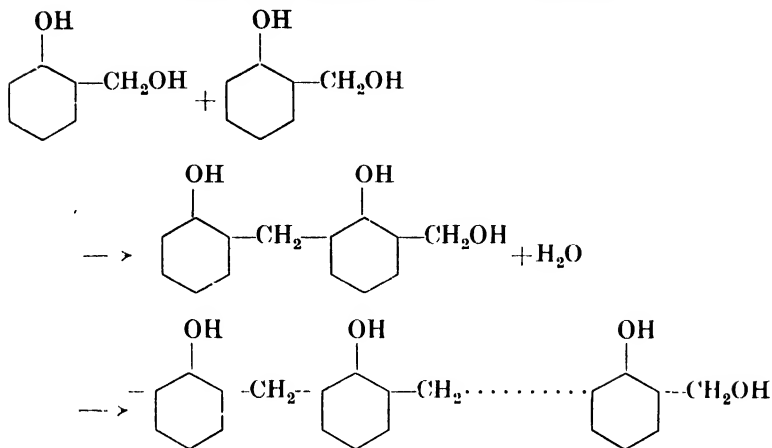
When formalin is used it is probably more correct to write the reaction thus:



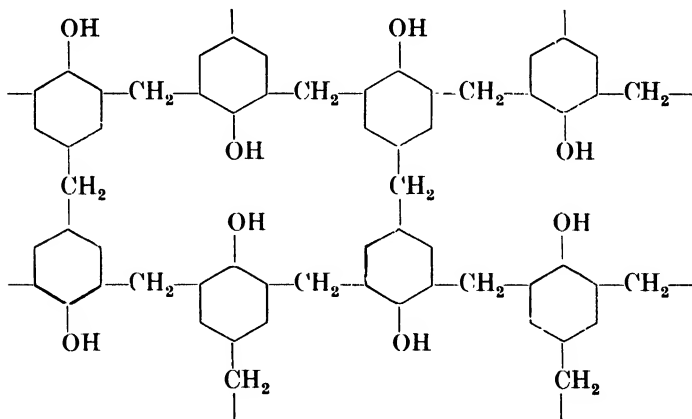
There is an important difference in the way in which the reaction between phenol and formaldehyde proceeds according to whether an acid or alkaline catalyst is used; although this seems to have been recognized in a vague manner for some time, it was first clearly stated by Weith¹² that with acids condensation products of the type



On a 1:1.5 phenol:formaldehyde ratio using an alkaline catalyst, after the production of saligenin the next stage is believed to be substantially the formation of chain compounds with methylene linkages, chiefly *ortho* to *ortho*, although some *ortho* to *para* and *para* to *para* most probably take place.



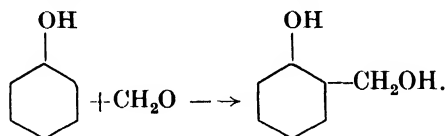
At this stage the resin is soluble in alcohol acetone and aqueous alkali. On further reaction the resin thickens and eventually becomes hard and infusible, a condition which is generally agreed to be associated with cross-linking to give a three-dimensional network arrangement, conveniently indicated by the following ideal structure:¹³



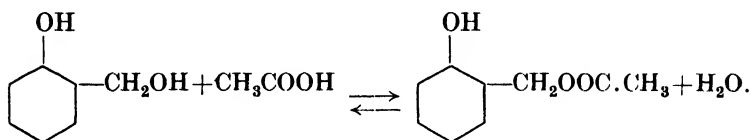
According to J. H. de Boer,¹⁴ if all of the possible primary valency links in a phenol-formaldehyde resin are actually formed, the theoretical tensile strengths of the thermo-hardened resin should be about 4,000 kg./mm.² If, however, the resin consists of irregular masses (macromolecules) of fully combined phenol and formaldehyde molecules linked together by van der Waals forces, the theoretical tensile strength should be about 35 kg./mm.² The value found experimentally is only about 7.8 kg./mm.²

R. Houwink¹⁵ in his 'Lockerstellen' theory (cf. Chapter XVI) has suggested that flaws in hardened phenol formaldehyde resin occur because not all of the possible methylene bridges are formed, a hypothesis which is comprehensible when it is realized that not all of the benzene nuclei lie in the same plane. Also the presence of occluded reaction products, water molecules for example, may give rise to holes in the resin structure. These flaws would have the effect of preventing some of the possible reactive points from getting in contact one with another, and hence the discrepancy between the values of the theoretical and observed tensile strength.

*Special reactivity of formaldehyde.*¹⁶ When formaldehyde is reacted with phenol the chief initial product is the methylol compound, saligenin, that is, hydroxy-benzyl-alcohol:

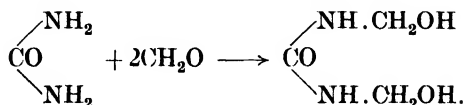


Since this compound contains a primary alcohol group, it might be expected that, on treatment with an equimolecular proportion of acetic acid, the following esterification reaction would take place:

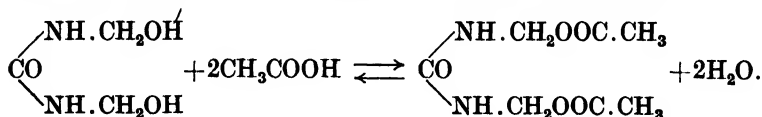


It is a commonplace, however, that the reaction of saligenin with an acid, acetic acid for example, leads to the formation of resinous products through a reaction involving the methylol group of one saligenin molecule with nuclear hydrogen of another saligenin molecule.

When formaldehyde is reacted with urea under appropriate conditions, the product obtained is dimethylol urea:



Since methylol groups, that is, primary alcohol groups, are present, it might again be expected that the following esterification reaction would take place with the equivalent amount of acetic acid:



Again, it is well known that the reaction of dimethylol urea with an acid, acetic acid for example, leads to the formation of resinous products by a reaction involving the intermediate production of methylene groups.

It would appear, therefore, that primary alcohol groups obtained as the result of the reaction of formaldehyde with another compound have a different reactivity from ordinary primary alcohol groups. It is probably more correct to say that those compounds (phenol and urea, among others) which have the property of forming primary alcohol groups with formaldehyde, confer a special reactivity on those primary alcohol groups.

This is an interesting phenomenon in view of the fact arrived at empirically that the only thermo-setting synthetic resins with curing time rapid enough for mass production plastic moulding are those made with formaldehyde as one of the reactants.

REFERENCES

1. E. Field, E. H. Dempster, and G. E. Tilson, *Ind. Eng. Chem*, 1940, **32**, 489.
2. Technical Records of Explosive Supply, No. 6, *Synthetic Phenol and Picric Acid*, 1921.
3. Durez Co, U S A, *Brit. Plastics*, 1940, **12**, 139, 237; *Chemical Industries*, 1940, 522.
4. M. Klar, *Chem. Ztg*, 1935, **59**, 741.
5. J. F. Walker, *Ind. Eng. Chem.*, 1940, **32**, 1016.
6. H. W. Homer, *Chem. Ind.*, 1941, 417.
7. *Helv. Chim. Acta*, 1925, **8**, 41; Pratesi, *Gazetta*, 1934, **14**, 139.
8. H. Freundlich, *J. Oil Col. Chem. Assoc.*, 1935, **18**, 64.
9. L. H. Baekeland, *Ind. Eng. Chem* 1909, **1**, 149.
10. L. H. Baekeland and H. L. Bender, *ibid*, 1925, **17**, 225.
11. N. J. L. Megson, *J.S.C.I.*, 1938, **58**, 136 T.
12. R. E. Burk, H. E. Thompson, A. J. Weith, and J. Williams, *Polymerization*, p 217 (Rheinoold Publishing Corporation, 1937).
13. N. J. L. Megson, *J.S.C.I.*, 1933, **52**, 420 T; M. Koebner, *Brit. Plastics Year Book*, 1934, 67.
14. *Trans. Faraday Soc.*, 1936, **32**, 10
15. *Ibid.*, 128.
16. C. A. Redfarn, *Brit. Plastics*, 1941, **13**, 145, 14.

II

COMMERCIAL PRODUCTION OF PHENOLIC MOULDING POWDER; MOULDING OPERATIONS; PRODUCTION OF LAMINATED MATERIALS; SYNTHETIC RESIN BONDED PLYWOOD AND CAST PHENOLIC RESIN

Commercial Production of Phenolic Moulding Powder.

The plant used in the production of Novolak and one-stage resins consists essentially of a cup-shaped reaction vessel commonly known as a 'digester'. The digester is generally made of copper, although stainless steel or nickel may be used. The vessel is jacketed and fitted with supply pipes and cocks so that steam-heating and water-cooling (in case the reaction gets out of hand) can be obtained. At the bottom of the digester there is a large bore cock, running through the jacket into the reaction vessel, through which the finished resin can be discharged. The lid of the digester is flanged and bolted to a similar flange on the digester to give an air-tight joint. In the lid there are two glass windows, one for shining in a light and the other for visual inspection. In addition there is a charge hole with cover fitted with wing bolts. Through the centre of the lid there is an

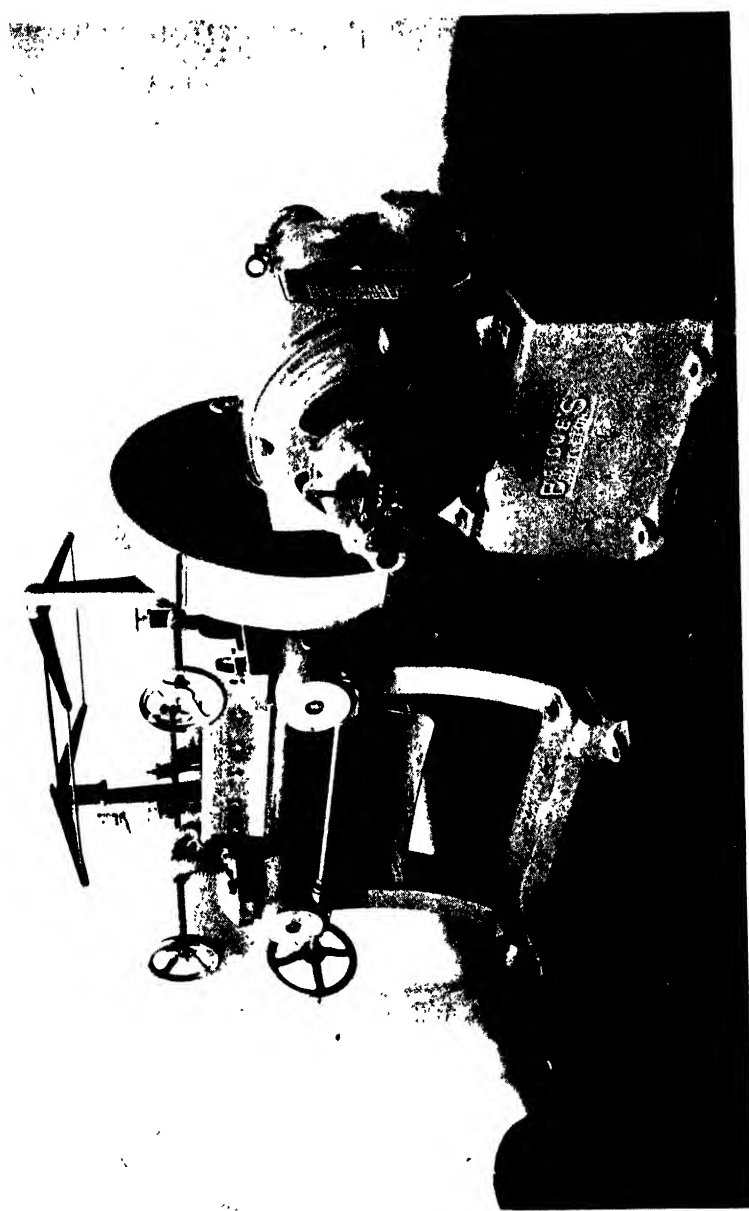


FIG. 10. Rollers for P.-F. Moulding in Powder Manufacture

anchor stirrer running through an air-tight gland. Other fittings to the lid are a gauge registering pressure and vacuum, a pressure safety-valve, a long hollow thermometer socket, and a hand pressure release cock. A condenser is fitted to the lid and usually arranged so that it can be used either for refluxing or distilling.

In making a Novolak resin the charge of phenol formaldehyde and acid catalyst is run into the vessel, boiled under reflux for a standard time, and then submitted to vacuum distillation. The end-point of the distillation is determined by breaking the vacuum and inserting a dip-stick through the charging hole. On cooling the dip-stick in cold water the resin should flake off readily. The resin is run out into shallow trays and allowed to cool. In order to obtain a uniform product the batches of resin are blended.

In the production of moulding powder the resin is roughly ground and cold-mixed, preferably in a large rotary mixer with an equal weight of 80-100-mesh wood flour, about 12 per cent. *hexa*, about 1 per cent. mould lubricant (e.g. stearic acid), colouring matter, a little furfural or tricresyl phosphate as plasticizer, and generally a little lime or magnesium hydroxide.

Batches of this cold-mixed coarse powder are then given a heat treatment at about 95° in a Bridge-Banbury mixer, which consists essentially of two heated rotors running in an enclosed heated body.

The object of this heat treatment is to advance the resin component as near to the Bakelite C condition as is consistent with leaving the resin with enough flow to fill the mould in the subsequent hot-pressing operation. The Bridge-Banbury treatment is stopped short of this point, the final adjustment of flow being carried out on heated rollers. (Cf. Fig. 10.) The use of the Bridge-Banbury mixer is a fairly recent modification: originally both mixing and cure adjustment were carried out on the rollers. In some quarters this method is still favoured.

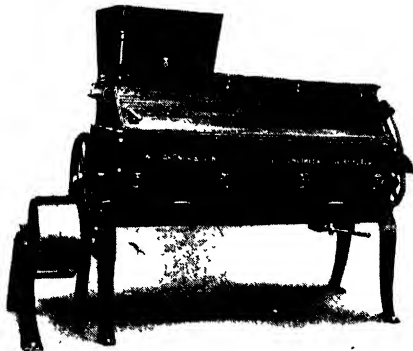


FIG. 11. Gardner Sifter and Blender

The blanket of material obtained from the rollers is cooled, crushed to coarse fragments, and disintegrated to give moulding powder.

Moulding powder made in this way is usually blended in a rotary mixer in as large batches as convenient in order to obtain uniform material. Cf. Fig. 11.

By reason of the colour instability of phenol, moulding materials from it can be made only in dark colours, black and brown being the colours most used. Rich dark shades in red, blue, and green are used to some extent, and mottles resembling certain kinds of wood are obtained by moulding roughly mixed powders of different shades of brown.

Asbestos-filled moulding powders for heat-resistant mouldings are made in a similar manner to that used for wood-flour filled powders; a rather lower proportion of short-fibred grey asbestos is used, since asbestos is merely covered by resin and not impregnated like wood flour.

Mineral fillers such as powdered mica are used in moulding powders required to show a lower shrinkage factor—that is, a smaller difference between the dimensions of the mould and of the moulding produced.

Moulding material used for mouldings of high impact strength are made with pieces of cotton fabric as filler. In this case the resin, hardening agents, and dyes are mixed with the filler by solvent impregnation and subsequently dried at elevated temperature.

Moulding powders used for moulding round thick metal inserts require a high degree of flexibility, in order that the moulded material may accommodate itself to the stresses and strains which are set up on cooling owing to the metal and moulded material having different coefficients of expansion. Moulding powders of this type can be made from resins obtained from phenol formaldehyde and a fatty oil—for example, China wood-oil.

Uses. By far the greatest use of phenolic moulding materials is for electrical insulation components. Other typical uses are: asbestos-filled material for heat-resistant articles, such as ash-trays; insulators for electrical heating apparatus; cloth-filled material for fishing-reels, door knobs, bottle closures, radio-cabinets, and the like.

Moulding Operations.

Phenolic moulding materials as supplied are in such a condition that the resin component requires for thermo-setting the minimum hot-curing time consistent with the ability to flow and fill the mould. Moulding material is put in a hot mould generally constructed in two parts (called the top and bottom forces) and submitted to pressure. The object of the pressure is to compress the hot moulding powder to a plastic mass which, being fluid, flows and fills the mould. During this flowing stage the resin in the moulding powder advances to the C stage and a small amount of vapour is liberated. The chief components of the vapour are ammonia from the *hexa* and the remnants of the water not removed from the material during processing. After the powder has fluxed and filled the mould the pres-

sure is maintained during the time required for the material to set hard so that the small amount of vapour liberated does not cause blisters to form on the moulding when the mould is opened.

The moulding temperatures used are from 300° F. (149°) to 350° F. (177°), and the pressures from 2,000 to 6,000 lb. per sq. in. on the moulding area. The temperature and pressure employed depend on the type of moulding material used and the kind of moulding being made. The length of curing time depends on the moulding temperature and on the thickness of the moulded piece.

For a thickness of $\frac{1}{4}$ in. at 320° F. (160°) the curing time on a standard wood-flour filled material is about 3 minutes and the time for thicker pieces is roughly proportionally longer. The influence of temperature on curing time is shown in the following graph,¹ which

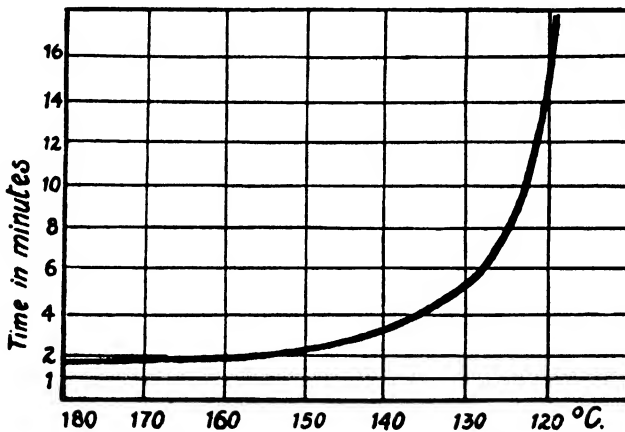


FIG. 12. Curing Time Graph

shows complete cure at 160° in 2 minutes, so the moulding was probably about $\frac{3}{10}$ in. thick. It will be noticed that the curing time is doubled when the temperature is dropped from 160° to 135°.

In commercial moulding, material in the form of powder, pellets, a tablet or a pre-form is put into the mould cavity, the mould being preferably fixed in the press (see semi-automatic moulding, on pp. 133, 140). The press is closed gently in order not to scatter the moulding material, and when shut the full moulding pressure is applied. With large mouldings the press is sometimes opened again after a short dwell of pressure and then rapidly closed. This opening is known as breathing or gassing, and the object is to let any volatile vapours escape, since, if left in, these vapours retard the rate of cure and may cause blisters. At the end of the curing time the press is opened and the moulding ejected, for example by means of a subsidiary ram acting through the bottom force. Moulds are generally designed to eject the mouldings from the bottom force. By running the

bottom force at a slightly lower temperature than the top, the moulding sticks to the bottom force.

Pellets, Tablets, and Preforms.

For the production of pellets the powder is fed into a pelleting machine which cold-presses the powder into a *pellet* of a definite weight, depending on the diameter and setting of the punch in the machine. A definite number of standard-size pellets is required for a given mould cavity. A *tablet* is really a large pellet of standard dimensions, but of such a size that one tablet makes up the loading charge for one mould cavity. A *pre-form* is a cold-pressed compacted mass of powder of the right charging weight and approximating in shape to the shape of the mould cavity. Pelleting, tableting, and pre-forming are carried out with the objects of reducing the bulk factor and avoiding the trouble of weighing out charges of powder. By reducing the bulk factor from $2\frac{1}{2}$ -3 for a powder to about $1\frac{1}{2}$ for a pre-form the charging space which must be allowed in the mould cavity is considerably reduced, a matter often of importance in mould design.

The object of pre-forming, as distinct from pelleting and tableting, is to distribute moulding material into the corners of an awkwardly shaped mould, and to prevent a sudden surge of plastic material which would break any delicate inserts. The use of powder or a tablet in such an awkwardly shaped mould would probably give a short moulding owing to the material being squeezed out of the mould before it could flow into the distant corners.

Finishing. The moulding obtained from the press has the high polish reproduced from the mould surface. It now requires 'finishing', that is, the removal of the 'fin' of flash material (see mould construction, pp. 133-6). In the mass production of mouldings finishing is often a troublesome procedure and may be more expensive than the actual hot-pressing process. There are no set methods for removing the flash. In some cases hand filing is necessary; for small articles tumbling barrels are often enough, whilst in other cases buffing wheels, belt and disc sanders may be used.

Phenolic Laminated Materials.²

The term 'laminated material' is applied to the products obtained by hot-pressing layers of resin-impregnated paper, fabric, or asbestos cloth. Laminated materials are supplied in sheet, tube, and rod form.

A one-stage ammonia catalysed resin is commonly used, and the resin is dissolved in methylated spirit to which 5 per cent. of acetone may be added in order to get a clear solution. The resin content of the varnish may be, for example, about 50 per cent. The properties of the varnish are checked and standardized by means of specific gravity and viscosity determinations, the specific gravity being a measure of the resin content and the viscosity a measure of the degree of polymerization of the resin.

The material to be impregnated with the varnish may be paper (Kraft, cellulose, or rag), duck, canvas, cotton cloth, or asbestos cloth.

In the impregnating process a roll of paper or cloth on a mandrel is unwound over a roller, through the varnish bath, and then over another roller with scraper or through special wiping rolls in order to remove excess varnish. The impregnated paper is then drawn through a long drying chamber heated by steam coils in order to

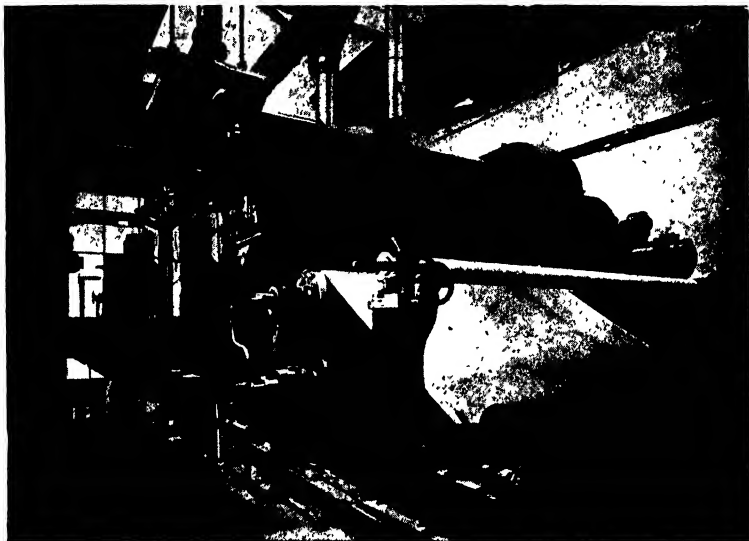


FIG. 13. Impregnating Plant

remove most of the solvent, which may be collected in a solvent recovery plant. A small amount of solvent is left in the paper, since completely dried impregnated paper is too brittle to handle. The tension and feed of the paper in the impregnating and drying machine are adjusted so that wrinkling and undue stretching are avoided.

In the next hot-pressing stage the surface of the material produced is determined by the surface of the plates between which it is pressed. Steel and copper plates with a high mirror polish, matt, or satin finish are used.

The dried impregnated paper is cut to size and made up into packets, the number of sheets in the packet determining the thickness of the finished material. The packets with their metal surfacing sheets are put between the daylight of a special multiple daylight steam-heated press, with the platens heated to 130–65°. The press is closed and a pressure of 1,000–2,000 lb. per sq. in. applied and the material cured for about an hour. The degree of drying of the impregnated material and the pressing conditions are adjusted so that there is the minimum of extrusion of resin round the sides of the platens.

At the end of the cure the material is cooled under pressure by

circulating cold water through the platens; this is necessary in order to prevent the residual solvent present from raising blisters. The material is then ejected, trimmed, and, if necessary, any surface scratches buffed out.

The resin content of the finished material is controlled at a pre-

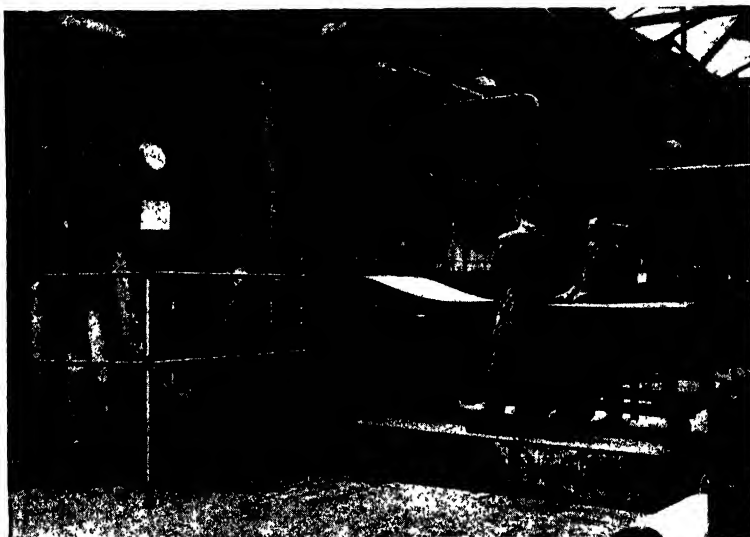


FIG. 14. Removal of Sheets from Laminating Press

determined value between 20 and 80 per cent. In general, high resin content gives better electrical properties and moisture resistance, and a low resin content better mechanical strength. Also paper-laminated materials have the best electrical properties, cloth-laminated materials the best physical strength, and asbestos cloth-laminated materials the best heat resistance.

Special types of laminated paper material with a high degree of flexibility are made for use in the punching method of preparing insulator parts in which the required shape and holes are punched out of thin laminated sheet. The flexibility is obtained by using a flexible resin made, for example, by combining a phenol-formaldehyde resin with an alkyd resin or a fatty oil.

The surface dimensions of laminated sheets are commonly 84 in. \times 36 in. The thickness of paper-laminated materials is from 0.004 in. to 2 in. and fabric-laminated materials from 0.008 in. to 2 in.

Laminated tubes are made by winding the impregnated paper or fabric over hot rollers, in order to soften the resin, and then wrapping tightly round a slightly tapered mandrel. The mandrel is turned between three rollers, the bottom two generally being heated and the top one spring-loaded. The final cure of the tube is effected by

oven-baking the tube on the mandrel, or by hot-pressing it in a steel mould, after which the mandrel is withdrawn. The production of moulded tubes is confined to small diameters up to 2 in., larger sizes usually being made by the rolling and baking process. Rods are made by rolling the impregnated paper or fabric on a wire which is then withdrawn and the orifice closed up during the subsequent hot-pressing in a mould. Rods may also be obtained by machining out of sheet materials, but in such rods the lamination lines show on the surface.

Other specialized types of laminated materials are cotton-cloth laminated bearings and brake and clutch linings made from asbestos cloth, which may contain strands of brass or zinc wire. The bearing materials are used with water as lubricant and are finding increasing industrial outlet, outstanding examples of which are bearings for roller mills and the tail shafts of ships' propellers, in place of *lignum vitae*.

General properties of laminated materials. The mechanical strength of laminated materials is high enough to make it for many purposes superior to wood and metal. For instance, it has 90 per cent. of the tensile strength of aluminium with only half the specific gravity. Laminated materials, particularly paper-laminated with high resin content, have good electrical properties.

Simple shapes, for example, a tea-tray with raised edges, can be produced by hot-pressing laminated paper and fabric materials. The materials are, however, generally shaped by machining, e.g. cutting, drilling and stamping, polishing, &c.

Uses of laminated materials. The earliest use, and still one of the most important, of laminated material is for high-voltage insulation. The high electrical strength, relatively low power factor, and resistance to oil, moisture and heat, have made laminated paper materials particularly suitable for the manufacture of switch-gear transformers, and telephone, radio, and television apparatus.

Silent gear-wheels (running in mesh with metal wheels) are machined out of fabric-laminated materials, which are also used for silent-running truck and trolley wheels.

Owing to their resistance to dilute acids, solvents, and—for one particular grade—alkalis, phenolic laminated materials are used in the construction of chemical plant.

Laminated paper sheet materials are obtainable in plain colours and in variegated effects: such materials are used largely for furnishing and decorative purposes, e.g. panelling, table tops, counter tops, doors, and the like. In one type of laminated-paper material the top sheet of paper carries a photographic reproduction of wood graining so that the finished sheet has an extremely close surface resemblance to wood. The production of such a material would appear to be a retrograde step in plastics development, since it stresses the use of plastics as substitute materials. Plastics are new, largely synthetic materials which are well able to stand on their own merits.

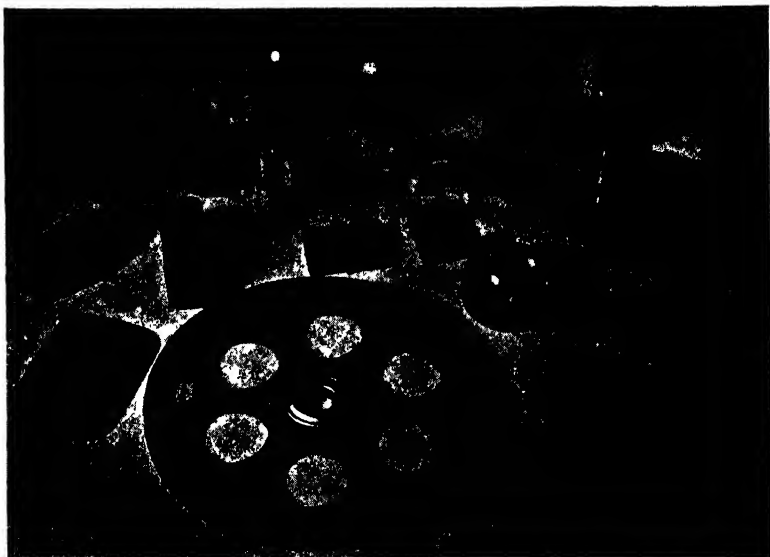


FIG. 15. Examples of Laminated Materials (Aircraft Components)

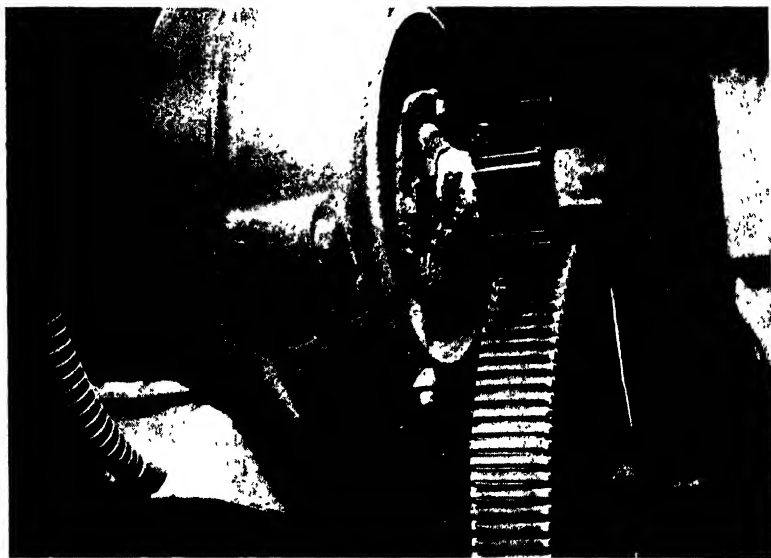


FIG. 16. Examples of Laminated Materials (Silent Gears)

Comparison of Properties of several different Types of P-F Laminated Sheet

<i>Physical properties</i>	<i>Typical high-grade paper laminated for h.t. insulation</i>	<i>Typical type of ordinary grade paper laminated for l.t. insulation and mechanical purposes</i>	<i>Special grade of paper laminated for tropical uses and h.f. insulation</i>	<i>Standard type of fabric-laminated material for gears and mechanical uses as specified in B.S.S. 668</i>	<i>Standard type of fabric-laminated material having high mechanical strength</i>
Ultimate tensile stress (lb. per 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. per 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. per sq. in. compression	1.2-1.8	1.0-1.6	1.0-1.5	2.0-2.5	2.6-3.6
Wrapping test	65-75	45-55	110-130	15-25	15-25
Specific gravity	1.31	1.38	1.33	1.34	1.34
Weight per cub. in.	21.5 gm.-0.76 oz.	22.6 gm.-0.80 oz.	21.8 gm.-0.77 oz.	22 gm.-0.77 oz.	22 gm.-0.77 oz.
Coefficient of expansion per °C. through laminae	0.00003-0.00009	0.00013-0.00017	0.00003-0.00005	0.00007-0.00011	0.00008-0.00011
Volume resistivity (megohms per cm. ³)	10 ⁷ -10 ⁸	10 ⁶ -10 ⁷	10 ⁸	10 ³ -10 ⁴	10 ³ -10 ⁴
Surface resistivity (megohms per cm. ²)	10 ⁴ -10 ⁷	10 ⁵ -10 ⁶	10 ⁷	10 ² -10 ³	10 ² -10 ³
Power factor at 800 cycles (per cent.)	1.5-3.5	2.5-4	1.5-2.5	20-40	20-40
Dielectric strength at 90° C. (volts per mil)	200-400	120-200	300-600	30-60	30-60
Dielectric strength at 20° C. (volts per mil)	400-600	350-450	400-700	80-120	80-120
Breakdown along laminae at 90° C.	30-40 kV.	20-30 kV.	70-100 kV.	5-7 kV.	5-7 kV.
Dielectric constant	3.4-5.7	5.7-6.3	4.2-4.5	9-11	9-11
MOISTURE ABSORPTION					
$\frac{1}{8}$ in. thickness	0.90 per cent.	3.5 per cent.	0.25 per cent.
$\frac{1}{4}$ in. "	0.60 "	2.1 "	0.15 "	$\frac{1}{4}$ in. 0.30 per cent.	$\frac{1}{4}$ in. 0.50 per cent.
$\frac{3}{8}$ in. "	0.40 "	1.1 "	0.09 "	$\frac{3}{8}$ in. 0.45 "	$\frac{3}{8}$ in. 0.45 "
$\frac{1}{2}$ in. "	0.25 "	0.40 "	0.06 "

Synthetic Resins in Plywood Manufacture.³

Plywood is composed of an odd number of thin slices of wood, termed veneers, bonded together with the grain in adjacent sheets running at right angles. A structure of this nature distributes the fibre strength of the wood, greatly reduces swelling and shrinkage, and eliminates the possibility of splitting of the material as a whole. The durability of such a composite material as plywood is largely dependent on the nature of the bonding medium. Formerly the common types of glue were used, giving rise to plywoods in which the glue lines were potential sources of weakness, particularly with regard to susceptibility to water penetration and mould growth.

Within the last nine years considerable attention has been given to the use of phenolic and urea resins as the bonding medium. The resins have been applied to the veneers as dry powders, in solution or emulsion and, more recently with phenolic resins, in 'film' form. The term 'film' is commonly applied to the thin sheets of paper impregnated with a special type of one-stage phenol-formaldehyde resin. Such films are interleaved between wood veneers and the whole assembly bonded in a press at 145° and 250-300 lb. per sq. in. pressure.

In the case of urea resins the most recent method appears to be to mix an aqueous solution of the resin with flour or other similar material and to apply this dope to the veneers by means of a spreading machine, the veneers being subsequently bonded by heat and pressure.

An important factor in obtaining the maximum adhesion with synthetic resins in plywood manufacture is the control of the moisture content before hot-pressing.

By using high pressures during the bonding operation there are obtained denser and harder materials in which the separate identities of the wood and resin apparently disappear.

Another development which is receiving considerable attention is the use of cold-curing synthetic resin as the bonding medium. Catalyst is added to the resin before doping the veneers, which are subsequently assembled and allowed to stand cold under pressure.

By using synthetic resins as the bonding media, plywoods are obtained with reduced swelling, shrinkage, and moisture transference, increased resistance to water and acid, better hardness and compressive strength, and resistance to mould growth. Plywoods of this nature are much superior to the original glue-bonded materials and are being used to a large extent in aeroplane construction. Other considerable uses in peace-time were in the manufacture of furniture, doors, counters, and so on, and in house and boat building.

Resin Impregnated Wood.⁴

A product distinct from synthetic resin-bonded plywood is that obtained by *thoroughly* impregnating seasoned wood veneers with phenol-formaldehyde resin, drying, and hot-pressing. In the material

produced in this way the wood and resin lose their separate identities and the result is a new product with interesting properties.

Beech and birch and sometimes spruce and acacia veneers from 14/1000 of an inch and upwards are used. After preliminary seasoning the wood veneers are processed under heat in a press to remove 'free' water. A batch of these dried veneers is loaded into a metal cage and an impregnating vessel is filled with the loaded cages. The vessel is then evacuated in order to complete the removal of any free moisture left in the wood. An alcohol solution of phenolic resin is added and pressure applied to the vessel. After thorough impregnation the veneers are removed and submitted to heat and vacuum in another vessel in order to remove the alcohol. Hot-pressing is carried out in multiple daylight steam-heated presses. The number of veneers for a definite thickness are packed between the platens. Hot-pressing reduces the thickness by 30 per cent. or more. The temperature and pressure used are carefully controlled in order to get uniform and consistent material. For thicknesses of 10 in. and over side supports are used in the platens so that the process becomes very similar to ordinary compression moulding.

Sitka spruce has high tensile strength and low compressive strength. Phenol-formaldehyde resin (C stage) has high compressive strength and low tensile strength. Spruce impregnated and bonded with phenolic resin has considerably improved and balanced properties. The increase in strength is accompanied by increase in s.g. which is influenced by the percentage of resin present and the curing pressure. The increase in s.g. produced by increase in pressure raises the tensile strength at a greater rate than the compressive strength, whilst the s.g. increase resulting from higher resin content raises the compressive strength at a greater rate than the tensile strength.

By differential impregnation, that is, by arranging that the resin content decreases from one end of the product to the other, the density can be varied from one end to the other. A similar result can be obtained by differential pressure, that is, by pressing between parallel platens a pile of veneers with the pile thicker at one end. Such differential materials are used in propellers which have to withstand high stresses at the hub with the stresses tapering off to zero at the tip.

Hot-pressed resin-impregnated wood has the appearance of extremely dense plywood and is from four to six times harder than ordinary hardwoods such as beech and oak. The s.g. is about 1.3 to 1.4, and in material with alternate veneers at right angles the average compressive strength is about 30,000 lb. per sq. in. The dielectric strength and resistance to acids and alkalis are good. Special technique and special tools are required for machining the material.

Hot-pressed resin-impregnated wood is used for end winding supports for generators, circuit breaker tension rods, terminal boards, end-rings for transformers, bus-bar supports, insulating fish-plates

for railway signalling, track circuit-block joints, silent-running gear-wheels, water-lubricated bearings, acid-resistant chemical plant, and air-screw blades.

Cast Phenolic Resins.

The earliest attempts at the preparation of phenol-formaldehyde resins were in the direction of what are now known as cast phenolic resins. These materials are obtained primarily as thick syrups which are then hardened by baking in open moulds at atmospheric pressure.

The early cast resins were brown in colour and apt to be brittle, so did not have any appreciable commercial development. The successful development of these resins as tough products of pale colour and fairly good light stability was accomplished by F. Pollak and the Catalin Corporation. The improved properties are obtained largely by the use of a high formaldehyde ratio (2 to 2.5 formaldehyde to 1 phenol) and the addition of plasticizers.

As far as can be ascertained from the patents and other publications,⁵ the outline of the process is as follows:

A nickel plant consisting of a jacketed vessel, stirrer, condenser, and the usual fittings as described on pp. 117-18, is used. The reaction vessel is made of nickel, which is not attacked by phenol and does not catalyse colour development. One molecular proportion of phenol, 2.35 molecular proportions of 40 per cent. formaldehyde, and about 1.5 per cent. of caustic soda on the phenol content are heated under reflux either at the boil or for a longer time at 65° for a period found by experience to be sufficient to effect condensation without undue thickening of the liquor. The use of caustic soda and the high formaldehyde ratio delays considerably the separation of the liquor into two phases, so that a clear but rather yellowish homogeneous liquor is obtained.

The liquor is acidified with lactic acid which discharges most of the colour and then distilled up to 80° under a vacuum of 1 in. or less pressure. Prior to, or at the end of, the distillation about 10 per cent. of plasticizer on the resin content is generally added. Glycerol, glycols, and triacetin are among the plasticizers mentioned in the patents, but none of these appears to be used industrially. The distillation is continued until a thickish syrup of definite viscosity is obtained. This syrup is usually yellowish and so is tinted to a faint purple shade with dyes when transparent 'crystal' material is required. For white opaque material water is generally added or left in the syrup. On hardening this water is liberated in the resin as droplets of colloidal size, which reflect light and give an intense white opaque appearance. Variegated material is made by carefully mixing transparent and pigmented syrups of the same or different colours and carefully pouring the syrup into moulds. Moulds are made by dipping formers of the required profile into molten lead. The skin of lead is removed, used once as a mould, and then put back into the melting-pot.

Hardening is carried out in electrically heated ovens at 60-80° for

3 to 8 days. During this baking process the resin syrup is gradually converted into a gel, then to a brittle chippy material which is converted by further baking to a tough mass. Over-baking makes the mass brittle again.

When the castings in the moulds have reached the tough stage they are taken from the ovens and ejected by sharp hammer blows on the bottom of the moulds; a pneumatic hammer is often employed. At the tough stage at which cast phenolic resin baking is stopped the resin is slightly thermoplastic. This is an advantage, since rods of, say, dress-buckle profile can be readily sliced into buckle shapes if the rods are heated to 175–288° F.

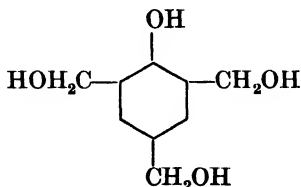
For the production of sheet material⁶, syrup is cast in block form and only partially hardened. Sheets of the required thickness are cut off on a machine similar to that used for celluloid or casein slicing and hardened and polished by hot-pressing between metal sheets.

As will be readily appreciated, by casting in lead moulds only shapes with a straight draw (preferably with a slight taper to assist ejection) can be made. For intricate shapes with re-entrant angles, glass moulds have been recommended, the glass being broken away when the resin is hard. An interesting development is the use of rubber moulds⁷ which enable reproductions of complex shapes such as statuary to be made.

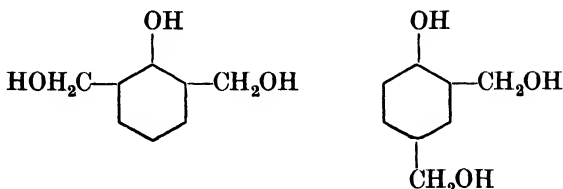
Chemistry of cast phenolic resins. The successful production of cast phenolic resin depends on the use of a high formaldehyde ratio and on the principle stressed by Weith,⁸ in that an alkaline catalyst is used in the first stage in order to load the phenol molecules with methylol groups. During the alkaline reaction some condensation probably takes place. Acidification, besides discharging the colour, brings about condensation leading to eventual hardening, this condensation taking place during distillation and baking.

Riesefeld⁹ has stated that the maximum amount of formaldehyde which can be combined with phenol under cast resin conditions is 2.5 mols. to 1 mol., the use of an excess of formaldehyde over this amount resulting in the presence of free formaldehyde in the hardened resin.

No work on the structure of cast phenolic resins appears to have been published. From Riesefeld's statement it would seem that the derivatives produced during the alkaline reaction of 2.5 mols. formaldehyde with 1 mol. phenol consist of equimolecular proportions of trimethylol derivatives:



and mixed dimethylol derivatives:



This view is confirmed by Thompson,¹⁰ who states that there are two or more formaldehyde molecules attached to the phenol ring in the *ortho*, *ortho'*, and *para* positions.

Condensation of these resin precursors apparently involves reaction of *meta*-hydrogen atoms in the phenol nuclei. It is difficult to conceive, on current theory, how else the high formaldehyde ratio can be accommodated. However, an alternative scheme of reaction can be visualized in which the phenolic hydroxy-group enters into the reaction. This contention was originally made by Baekeland in the early days of phenolic resin chemistry.¹¹ There is a trickle of experimental evidence appearing in the literature, notably that of Petrov and Ustinov,¹² in support of the view that the phenolic hydroxy-group takes part in phenol-formaldehyde resinification reactions—a state of affairs not countenanced by the simple *ortho*, *ortho'*, *para* reactivity hypothesis of thermo-setting.

Petrov and Ustinov report that diazo-methane, the most powerful methylating agent known, fails to methylate resites.

Properties and uses. Cast phenolic resin is reasonably light-stable, but specimens do show slight yellowing on ageing. It has s.g. 1.27–1.33; tensile strength of 3–5,000 lb. per sq. in., and water absorption 0.01–0.05 per cent. on 48 hours' immersion.

Cast phenolic resin is used chiefly for decorative and 'art' utility articles: for example, beads, umbrella handles, knife handles, shaving-brush handles, buttons, buckles, door knobs, &c.

REFERENCES

1. *Br. Plastics Year Book*, 1934, 88.
2. B.P. 220,043; E. H. Halls, *Br. Plastics Year Book*, 1933, 119; *Br. Plastics*, 1938, 11, 16, 306; G. H. Clark, *Modern Plastics*, 1938, 16, 2,200; Bayer, *Modern Plastics*, 1939, 17, 2,412; Bakelite Laminated Booklet, 1937; *Br. Plastics*, 1938, 10, 112, 186.
3. *Modern Plastics*, 1938; C. A. Redfarn, *Br. Plastics*, 1939, 11, 124, 191.
4. H. N. Hart, *Br. Plastics*, 1941, 13, 146, 154; Anon., *Plastics*, Feb. 1940.
5. B.P. 267,901, 290,963, 312,905, 357,276, 440,043, 440,959, 488,183, 488,184; Judgment of United States District Court, In Equity, No. 7,299, 18 July 1935.
6. B.P. 318,806, 353,870; *Br. Plastics*, 1938, 9, 106, 534.
7. *Modern Plastics*, 1938 and 1939.
8. See p. 114.
9. *I.P.I. Trans.*, 1939, 8, 15, 35.
10. *Modern Plastics*, 1939, 17, 2, 30.
11. E. Baekeland, H. L. Bender, *Ind. Eng. Chem.*, 1909, 1, 158; 1925, 17, 225.
12. *From. Org. Chim.*, 1936, 1, 216; *Ann. Rep. S.C.I.*, 1937, 22, 477.

III

ELEMENTARY MOULD DESIGN; MOULDING PRESSES; SPECIAL MOULDING PROCESSES (MOULDED COFFIN PROCESS, AUTOMATIC MOULDING); HEATING OF MOULDS AND HYDRAULIC PRESSURE; TRANSFER MOULDING AND EXTRUSION OF THERMO-SETTING MATERIAL

Moulds.

The moulds used in thermo-setting moulding are generally made from hardening steel which, after machining, is heat treated. Stainless steel is preferable for use with urea-formaldehyde materials. The moulding surfaces should be well polished and preferably chromium-plated, because the moulding material reproduces faithfully even the finest markings on the mould surface. According to their mode of use, moulds are classified as portable (or hand moulds) and semi-automatic moulds.

Portable moulds are lifted in and out of the press by the moulder, and the opening of the mould and removal of the moulding (known as stripping) is carried out by hand, sometimes with the aid of a small hydraulic stripping press. Such moulds are heated by direct contact with the press platens.

Semi-automatic moulds are fixed in the press and the moulding is ejected by devices incorporated in the construction of the press.

Moulds are classified as positive, flash, and semi-positive, according to the manner in which they are designed to reach their final state of closure under moulding conditions.

Positive mould (for illustration see Figs. 17 and 18). This type usually consists of three parts, a top force, a bottom force, and the

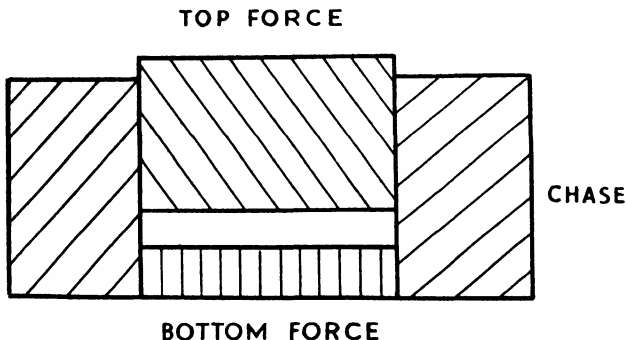


FIG. 17. Simple Positive Mould

outer retaining piece known as the chase, bolster, or collar. The top and bottom forces should be a tight sliding fit in the chase, and moulding material ought not to any appreciable extent be forced between the forces and the chase during moulding. With a positive

mould the exact moulding charge must be weighed out, since no provision is made for the escape of surplus material. An advantage of the positive mould is that following pressure is obtained on the

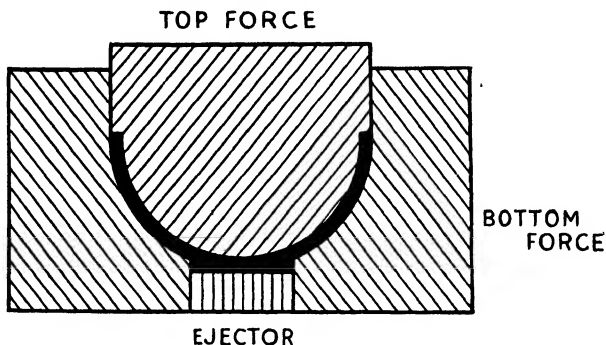


Fig. 18. Positive Mould to produce a Bowl

moulding all through the hot-pressing operation, so that well compacted mouldings are obtained. Ejection of the moulding is frequently effected by pushing the bottom force right through the chase.

Positive moulds are not used to any great extent in thermo-setting moulding on account of the exact weighing proviso and because they rapidly show signs of wear under moulding conditions. The sides of the chase and forces easily get scored during ejection by being driven past hardened fins of material which are inevitably produced in the chase as soon as the mould shows the slightest sign of wear.

Flash mould (Fig. 19). The flash mould consists essentially of two parts, the top and bottom forces, and since the forces do not fit into each other and have no retaining chase, dowel pins are used to keep the mould in alignment. All round the moulding cavity on each force there is a flat rim known as the flash area, each rim being complementary to the other. Under moulding conditions the mould is slightly over-charged and under pressure the excess material is extruded between the rims as a flash fin. When the surplus has been extruded the moulding is cut off at the flash area. On ejection the moulding is obtained with a thin fin of flash all round it. Since during the last stages of moulding the full pressure is supported by the flash rims, the expedient is often adopted of providing the mould with pads to take the pressure when the flash has attained a predetermined thinness so that undue wear of the flash rims is prevented.

The flash mould has the advantage over the positive mould of not requiring an exact moulding charge to be weighed out, but it has the disadvantage that following pressure cannot be applied to the moulding during the final stages of the cure to follow up the slight shrinkage that takes place as the result of the polymerization

of the resin component. In consequence slight porosity, especially round the edges under the flash scar, is often apparent in mouldings from a flash mould.

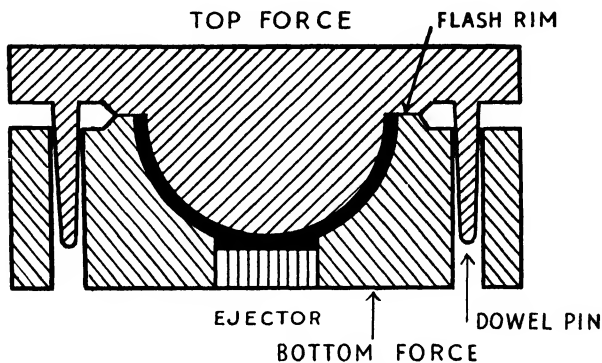


FIG. 19. Flash Mould to produce a Bowl

Semi-positive mould (see Fig. 20). The type of mould most used in modern moulding practice incorporates to some extent the features of the positive and flash moulds and is known variously as

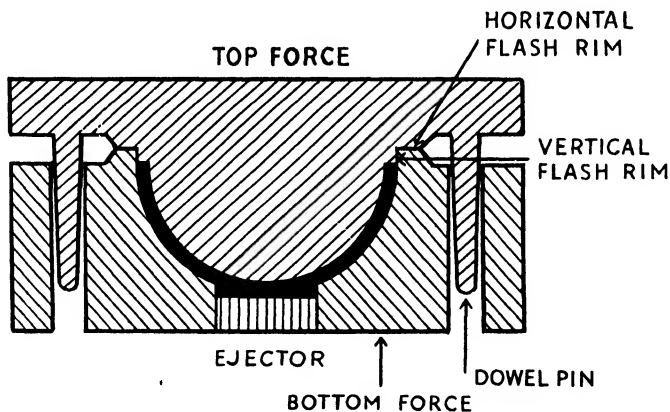


FIG. 20. Semi-positive Mould to produce a Bowl

the semi-positive, semi-flash, or positive-flash mould. The term 'semi-positive' seems to have the most adherents. This type of mould is similar to the flash mould in that it is basically composed of two parts, the top and bottom forces, but the top force is designed to project a short distance into the bottom force, so that positive follow-up pressure is exerted during the final closing of the mould whilst the final amount of surplus material is being extruded.

When small mouldings are being produced in quantity, multiple

cavity moulds which may have over two hundred moulding cavities are used, each cavity being, for example, a small semi-positive mould.

Split mould.

For the production of mouldings with re-entrant angles, such as a bobbin or egg-cup, a mould which splits vertically is used so that the moulded article can be ejected. The two halves of the split mould may be held together in a bolster or used in an angle press. A top and bottom force are generally used in conjunction with the split body.

Moulding Presses.

Practically all of the moulding of thermo-setting materials is carried out in hydraulic presses; mechanical presses (operated by screw and pinion, eccentric or toggle action) are not really suitable for the operation. In modern moulding practice the press has three functions to perform:

- (1) To apply the high pressure necessary to make the hot plastic material flow and fill the mould.
- (2) To compact the plastic mass into a solid non-porous moulding.
- (3) To pull the mould apart and eject the moulding.

In the course of the last fifteen years presses used for the moulding of thermo-setting materials have been considerably modified in order to adapt them to the requirements of modern mass production of mouldings from quick-curing materials. The modern moulding press has been evolved from the simple up-stroke press used in the rubber industry.

Simple up-stroke press. (Figs. 21, 22, 23). The simple up-stroke press is the type originally used. It consists essentially of four sturdy pillars to give rigidity, the pillars being anchored in the base which carries the hydraulic cylinder. A ram moving through a gland in the cylinder head is fixed to the movable table which is constructed with guides enabling it to slide smoothly up and down the pillars. At the top of the pillars is the fixed head of the press, held in place by collars, and heating platens are fixed to the top of the moving table and to the under side of the fixed head. The space between the platens, when the press is opened to its fullest extent, is known as the daylight. The cylinder is connected to a two-way valve which can be opened to hydraulic pressure, thus causing the press to close: by shutting off the hydraulic pressure and opening the valve to waste, the table of the press falls under gravity and discharges the water from the cylinder.

Under moulding conditions the pressure obtained with a hydraulic press is steady and regular and provides the follow-up pressure necessary in thermo-setting moulding. Mechanical presses are not really capable of giving this essential follow-up pressure.

The simple up-stroke press can be used for all portable moulds

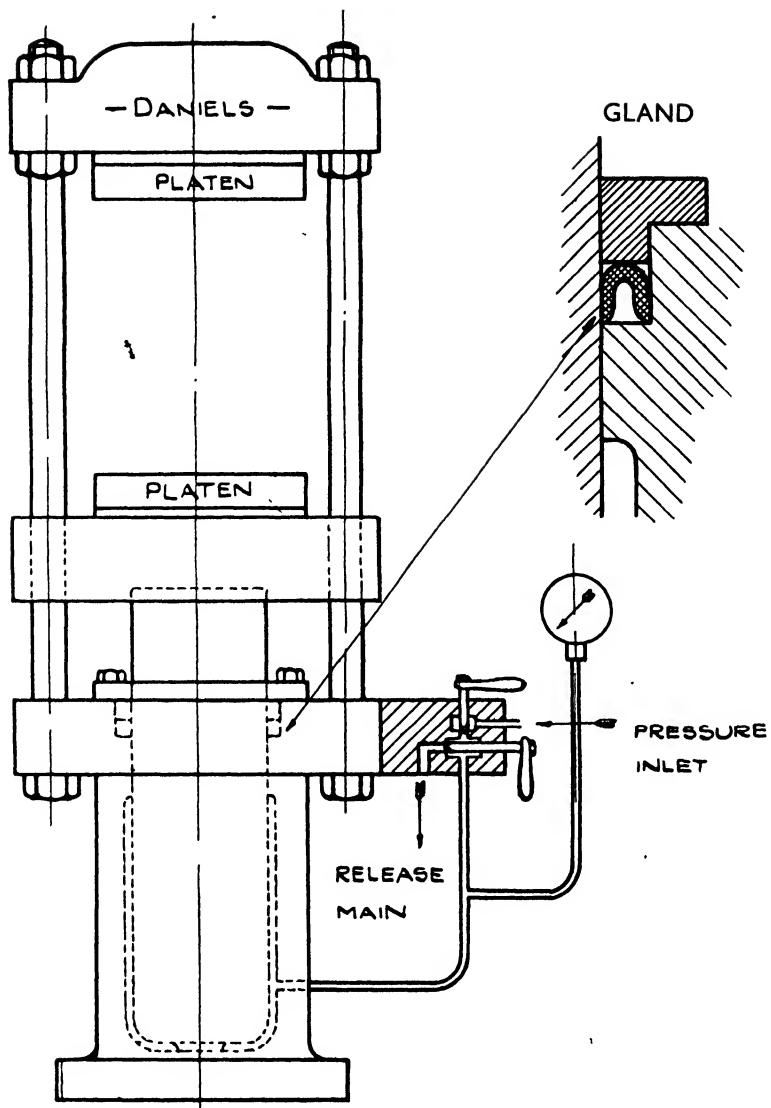


FIG. 21. Simple Up-stroke Press

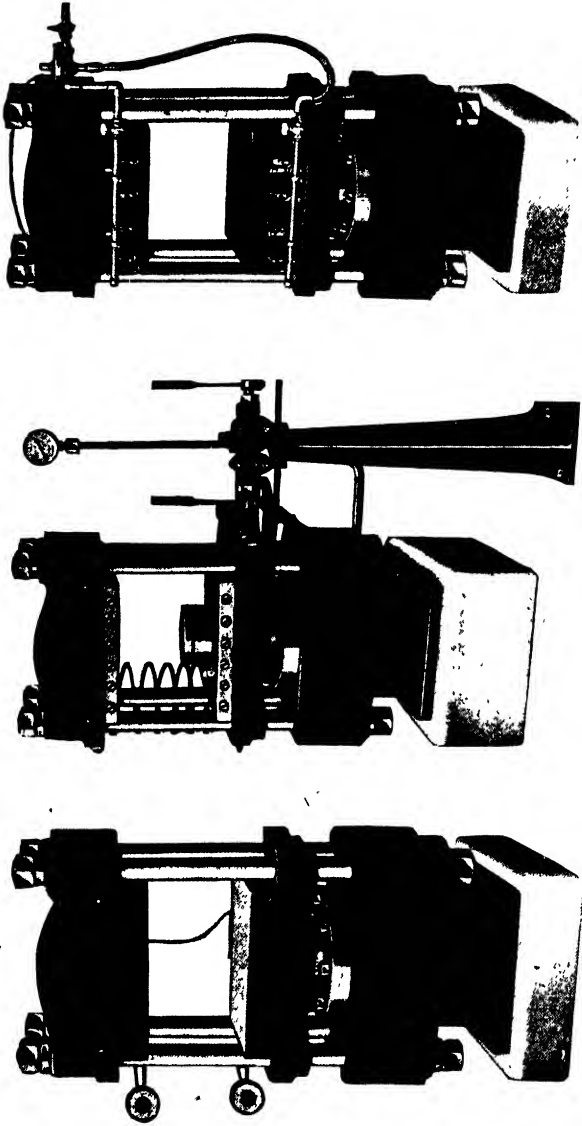


FIG. 22. Simple Up-stroke Presses for Electric, Steam, and Gas Heating

and for those fixed moulds which will open under the weight of the falling ram. Such a press was quite satisfactory for the slow-curing 'one-stage' moulding powders, which took so long to cure that the

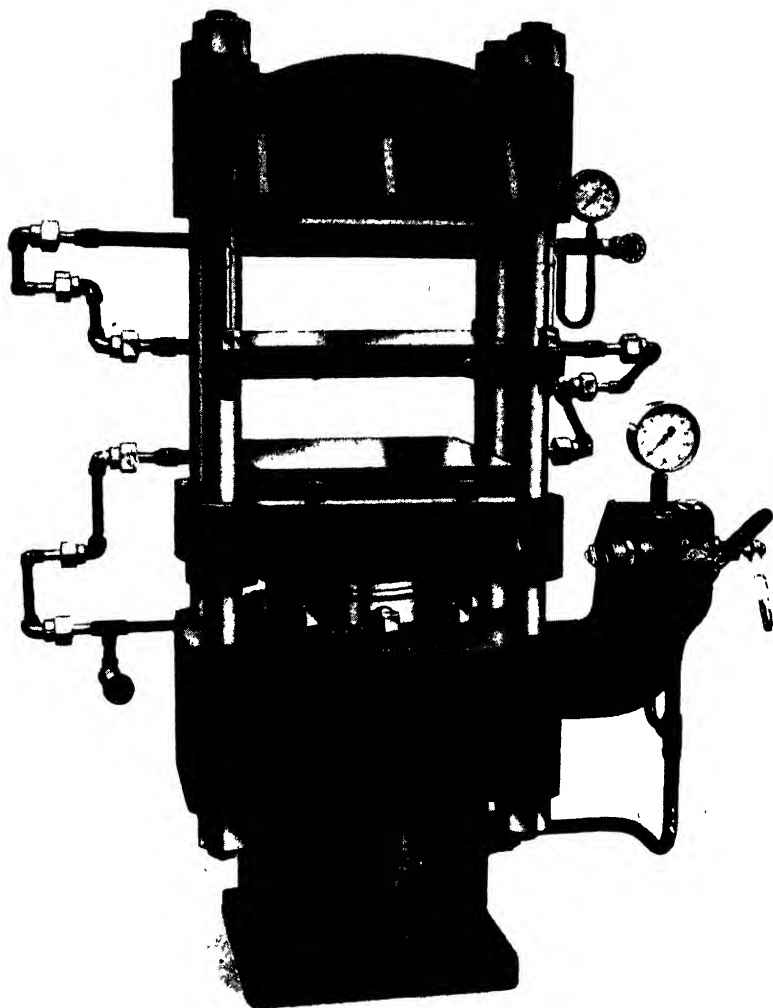


FIG. 23. Up-stroke Press with Floating Platen giving Two Daylights:
Knuckle-joint Steam Connexions shown

time taken up in the moulding cycle by loading and stripping the mould was short compared with the curing time. In order to increase

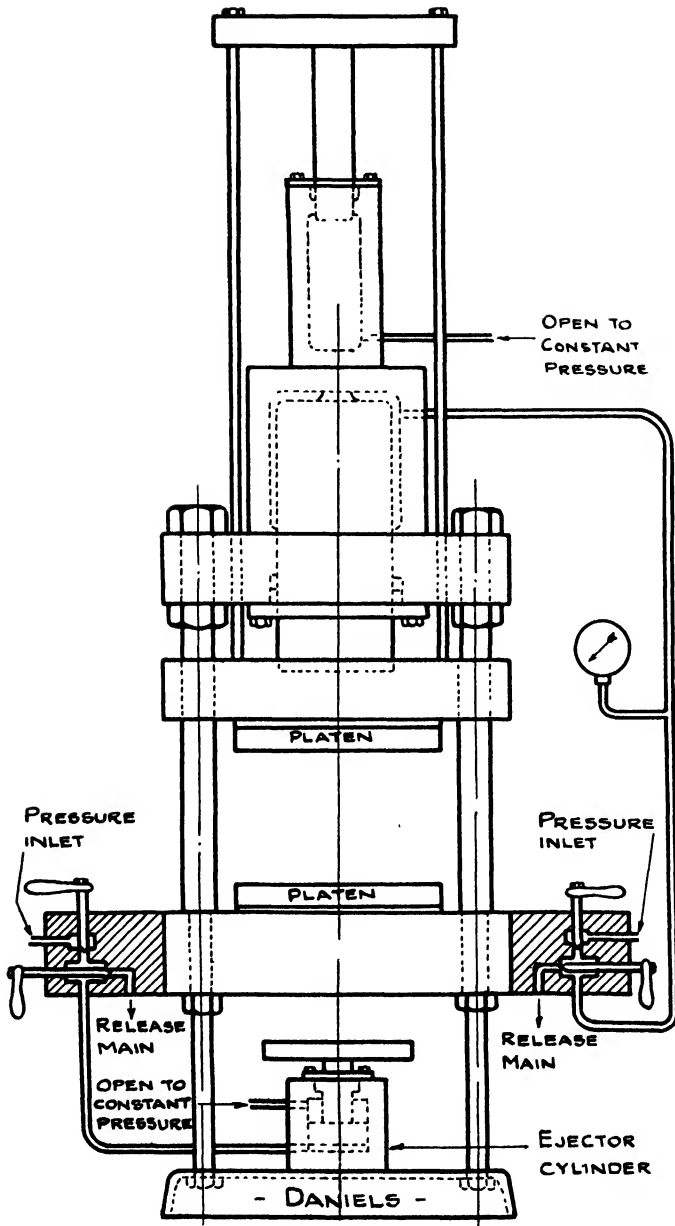


FIG. 24. Down-stroke Press with overhead Pull-back Ram

the rate of production it was often the practice to use presses with two or more daylight, so that two or more mouldings could be made during one pressing operation. During the pressing another set of two or more moulds was generally kept hot with the moulding powder ready alongside, so that moulding with the second set of moulds could be carried out whilst the first set was out on the bench being stripped.

Down-stroke presses. Round about 1925 the quick-cure two-stage phenolic moulding powders began to be used. Since the curing time is so short, the time taken in the moulding cycle for charging and stripping the mould became unduly long in comparison. This ultimately led to semi-automatic moulding in which the appropriate forces of the mould are fixed to the top and bottom platens of the press. Except with very simple moulded shapes, it is necessary to have some sort of ejector rod operating through the bottom platen to push the moulding out of the lower force of the mould. Whilst this can be done with an up-stroke press, the devices are rather cumbersome, since they involve cutting into the up-stroke ram.

The down-stroke press was devised to deliver the moulding pressure downwards by means of an overhead ram so that the space under the lower platen could be used for the ejection devices generally necessary in semi-automatic moulding. Obviously, with a down-stroke press an additional ram is necessary in order to open the press. The earliest type was made with an *overhead pull-back ram* (cf. Fig. 24). This ram is of considerably smaller diameter than the main pressure ram and is left always open to the hydraulic pressure. On the top of the pull-back ram there is a cross-head which is connected by sliding columns to the moving table fixed to the main down-stroke ram. When the main ram is opened to hydraulic pressure, its larger diameter enables it to overcome the upward pull coming from the smaller ram and the press closes. On opening the main ram to waste, the smaller ram automatically pulls up the table, thus emptying the main cylinder. Ejection through the bottom fixed table is effected by means of a cross-bar with appropriate gadgets fixed to the upper moving part of the press or more simply in later designs by means of a subsidiary ejector ram under the fixed table.

Such a press is wasteful of hydraulic pressure, since in the down stroke the pressure supplied to the main ram must be enough to overcome the upward pull of the pull-back ram and to give the required moulding pressure; also, by having one ram on top of the other, more head room is required. Presses of this type of improved design are still favoured in some quarters (Fig. 25).

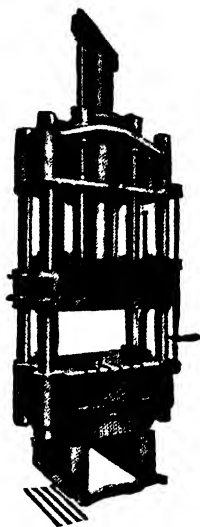


FIG. 25. Improved type of Down-stroke Press with overhead Pull-back Ram

The next development was the *down-stroke press with jack rams* (Fig. 26). In this press the opening is effected by means of small side rams, usually push-back. The side rams are sometimes left permanently open to the hydraulic pressure.

Efforts were next made to conserve the hydraulic pressure used in the moulding operation. During the greater part of its travel the main ram in a press is carrying out no useful work, apart from closing the mould and overcoming the pressure of the opening rams. High pressure is actually required only for the last inch or so of the stroke when the pressure is applied to the moulding material.

The *pre-filling down-stroke press* (Fig. 27) was designed so that it could be closed by low-pressure water and the high pressure applied merely to give a final 'nip'. Over the main ram there is a water tank which lets water into the main cylinder when a pull-down lever is operated. When the mould is charged the lever is pulled and water flows into the main cylinder from the overhead tank, and pushes the ram down. When the press is shut the lever is released and high-pressure water let into the main cylinder in order to give the 'nip'. After moulding, the hydraulic pressure is cut off, the cylinder opened to waste, and the pressure opened to the jack-rams in order to open the press.

The valving system on such a press is interlocked in order to prevent a wrong sequence of operations.

The latest development in moulding presses is the *pre-filling down-stroke moving cylinder press* (Figs. 28 and 29). In this press the ram is fixed to the press-head and the cylinder incorporated in the moving table. As will be seen from the illustrations, the use of a moving cylinder necessitates eight guides for the moving table on the columns instead of the usual four guides on the moving ram press. The use of eight guides gives a much steadier table with little, if any, tendency to rock. This is an important improvement when fixed semi-automatic moulds are used, since the greater part of the wear on such moulds is caused by faulty alignment of the top and bottom forces.

An eight-guide table could be constructed in a moving ram press, but this would involve the use of a ram double the length of that required in the moving cylinder press.

The calibre of a press is expressed as so many tons, that being the maximum pressure delivered by the main ram when connected to a supply line usually of 1 ton per sq. in.

Special Moulding Processes.

The largest plastics press used in this country is that used for the production of *moulded coffins*.¹ The inside dimensions of the coffin are approximately 6½ ft. long by 1½ ft. deep by 2 ft. wide at the broadest part. Moulded coffins are made in America, but these are moulded in separate sections (bottoms, sides, and ends) which are afterwards fixed together.

For moulding the body of the coffin a 4,000-ton single ram

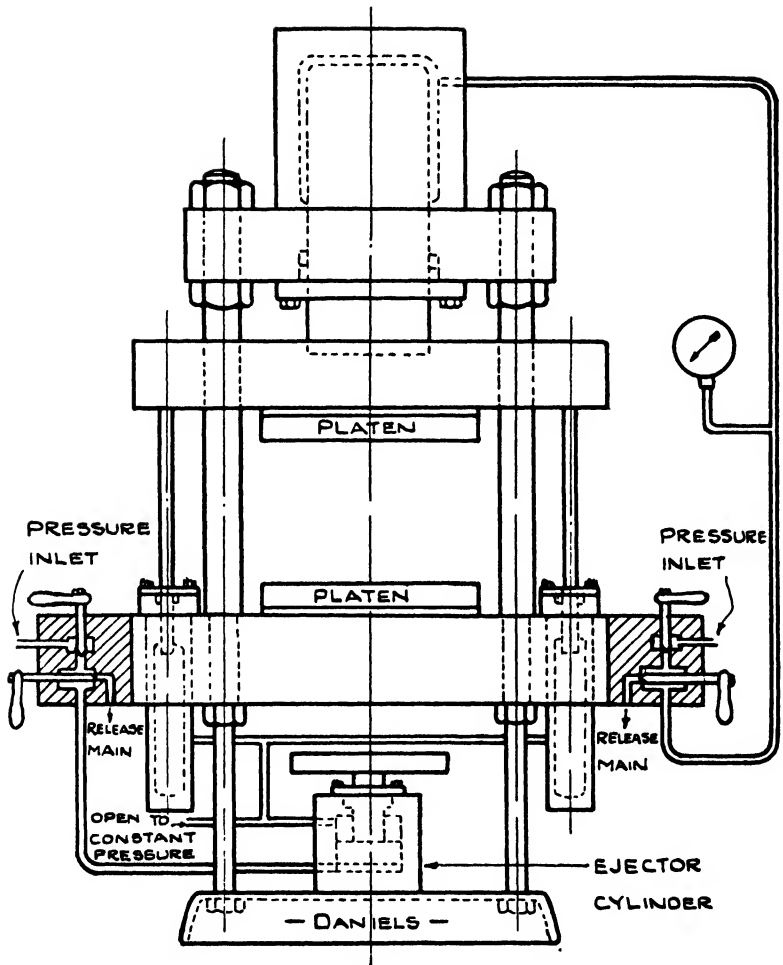


FIG. 26. Down-stroke Press with Push-back (jack) Rams

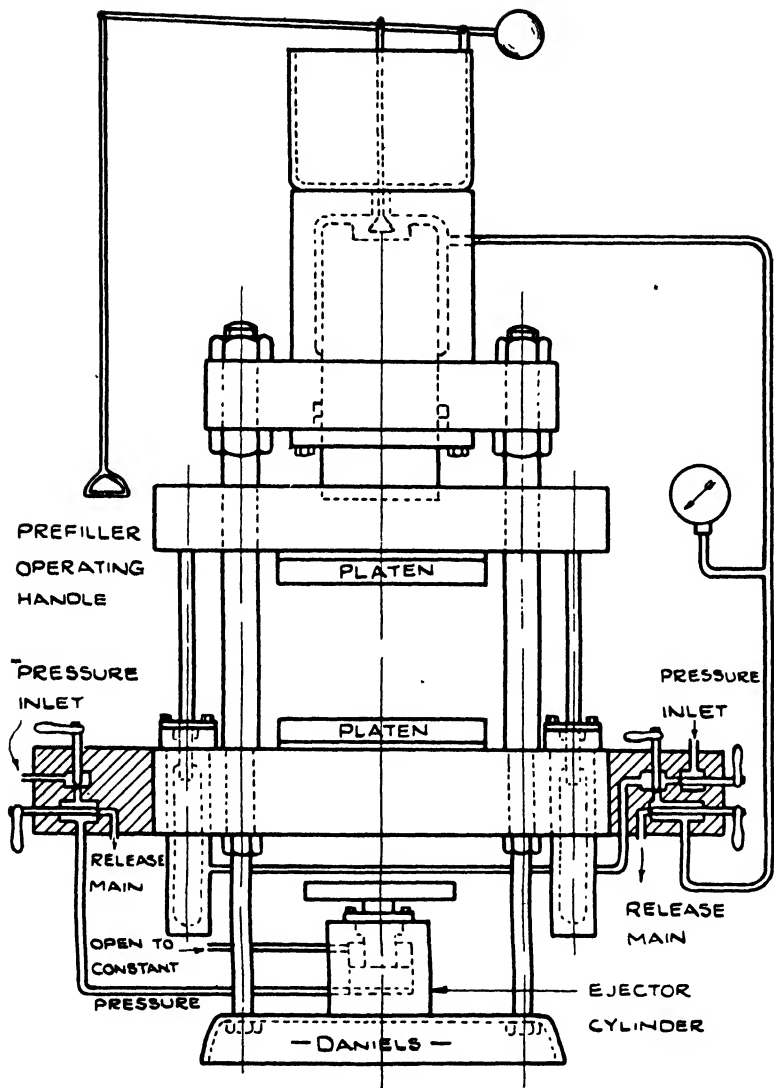


Fig. 27. Pre-filling Down-stroke Press with Push-back Rams

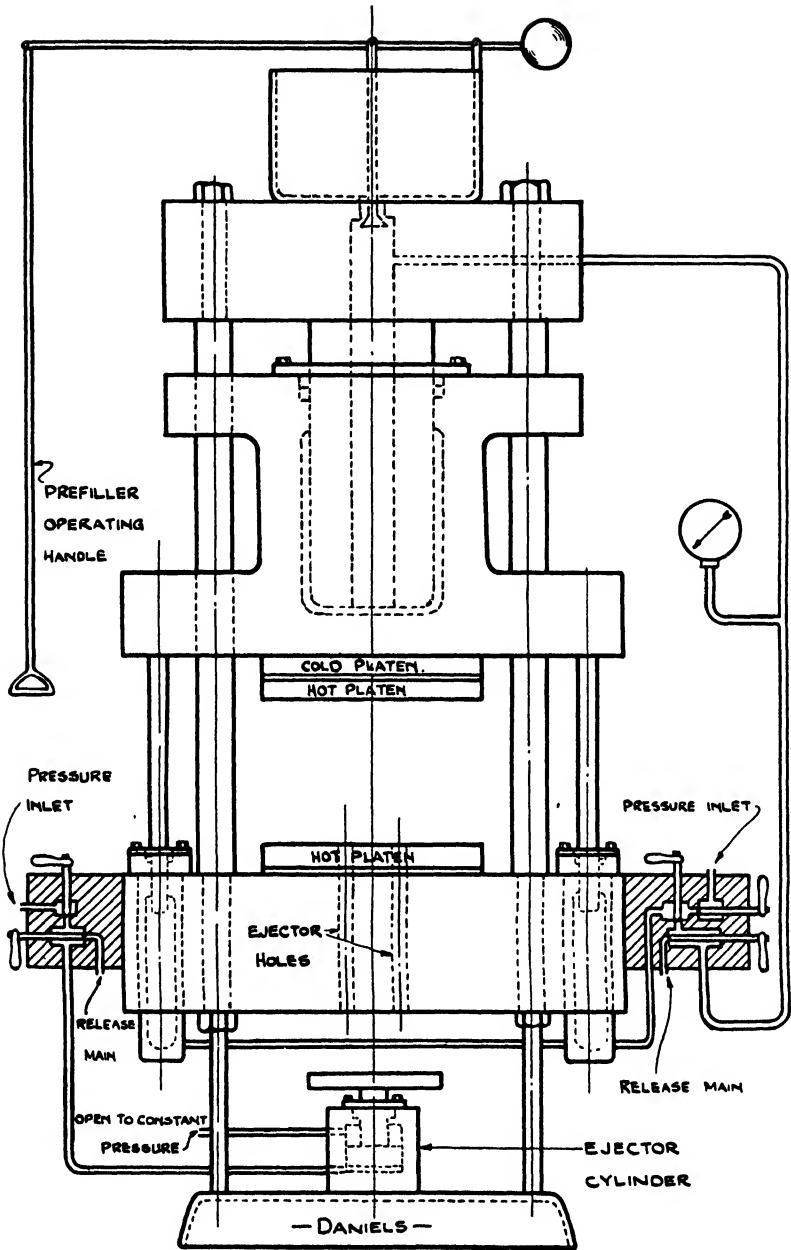


FIG. 28. Pre-filling Down-stroke Moving Cylinder Press



FIG. 20. Moving Cylinder, Pre-filling Press

pre-filling down-stroke press with pull-back jack-rams is used. Low-pressure water is used for pre-filling, but for the actual moulding pressure high-pressure water from a hydraulic intensifier is used. The mould is constructed, so that the two ends and the two sides can be moved in and out of position by means of double-acting rams. When in position the ends of the mould are keyed into the sides and thus locked into position during moulding. Ejection of the moulded coffin is carried out by means of two subsidiary rams acting through the bottom force. The mould is electrically heated and in operation spews out a vertical flash. The coffin lid is moulded in a two-ram 2,000-ton up-stroke press. In order to conserve hydraulic pressure the press is closed by means of two small-diameter side rams, the main cylinders being filled at the same time with low-pressure water. The mould is electrically heated and spews out a horizontal flash. The moulding is arranged to stick to the top force, from which it is liberated by subsidiary rams.

A standard (generally mottled) phenolic wood-flour filled material of easy flow is used at a temperature of 300–20° F. The moulding cycle is about 17–20 minutes for the coffin and 10–12 minutes for the lid.

Angle-press (Fig. 30). The angle-press is designed to provide pressure on the mould in two directions at right angles, and is used with split moulds.

The press has two main rams, each of which can be operated independently, as it has its own pull-back ram with cross-head and its own valve arrangements. The housing of the press may be cast in one piece, but more often the built-up steel-frame body is used.

The side or horizontal ram is used to hold the split-mould together and is generally designed to develop about 10 per cent. more pressure than the vertical ram in order to prevent the mould from opening.

Automatic moulding. Modern moulding practice is now carried out largely under semi-automatic conditions. The manual operations required are: putting the moulding material into the mould cavity, operating the valves, and lifting out the ejected moulding. Attempts have been made to get thermo-setting moulding on to an entirely automatic footing. As far as small mouldings are concerned, a considerable degree of success has been achieved with the Stokes and Lauterbach automatic presses.²

The Stokes automatic press is a completely self-contained unit and is essentially a 10-ton down-stroke press with compensating springs to give a steady pressure. By moulding at 1 ton per sq. in. the maximum horizontal surface area of the mouldings obtainable is 10 sq. in. A vertical flash mould with lands is used and the mould is fixed in the press. Electrical heating is employed, and to assist ejection the bottom force of the mould is run at a slightly lower temperature than the top force. Removal of the moulding from the bottom force is effected by means of pins working through the

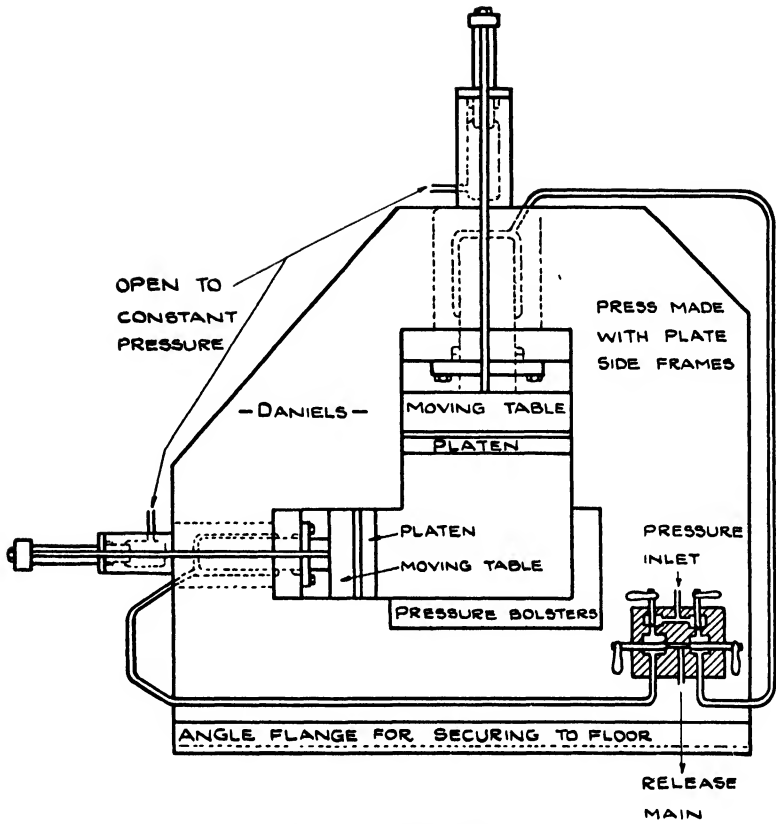


Fig. 30. Anglo Press

bottom force, the pins being operated by a cross-piece attached by columns to the main down-stroke ram. The moulding and flash are blown off the ejector pins by means of compressed air on to a tilting pan and from the pan to a receiving bucket. If the moulding is for any reason under weight the pan does not tilt, the press is stopped automatically, and a warning bell rings. The mould is charged through a chute with the correct adjustable amount of powder from a revolving cup working under the powder hopper. The sequence of operations, which are carried out entirely automatically and controlled by an elaborate self-acting switch-box, is:

- (1) Mould starts to close.
- (2) Charge of powder let into mould cavity.
- (3) Mould lands cleared by a blast of compressed air.
- (4) Full moulding pressure applied.
- (5) A short dwell of pressure.
- (6) Pressure released for 'gassing'.
- (7) Pressure reapplied and held for curing time.
- (8) Pressure released and press opened.
- (9) Moulding blown off with blast of compressed air.

The Stokes press is particularly suitable for the production of mouldings for which there is a steady but not very large demand: it is not suitable for multi-impression work. From an experimental point of view it is useful for determining how a moulding powder behaves on a long run.

The Lauterbach press³ is designed to give completely automatic moulding and is particularly suitable for the production of small articles such as screw-on bottle caps. The main body of the press consists essentially of a circular table which rotates in a frame. The table has twenty cavities equally spaced near the circumference, and these cavities carry the mould chases. Working through each chase there is an up-stroke hydraulic plunger with the bottom force of the mould attached. The top force is attached to a down-stroke plunger which is operated by means of a cross-piece and spring connected to the up-stroke plunger by means of a rod. The moulds are electrically heated. When working the correct amount of moulding material is automatically fed into one of the moulding cavities, the table moves on, and the next cavity is charged, and so on. As the table moves round each mould is progressively closed by means of the plungers, breathed (i.e. opened for gassing), and full moulding pressure applied. At the end of the cure the upper and lower plungers are withdrawn and the moulding sticks to the upper force. In the case of a screw cap the moulding is automatically screwed off the mould and, assisted by a compressed air-blast, falls into a chute leading into the receiving box outside the machine.

Provided that the machine is correctly set, all the operations are automatic and moulding continues without attention except for keeping the hopper charged with moulding material.

Heating Presses and Moulds.

Small moulds are heated by contact with heated press platens, but the larger moulds used in semi-automatic moulding are often heated directly.

There are four methods of heating, steam, hot water, gas, and electricity.

Steam heating. For steam heating saturated steam obtained from a Lancashire boiler is generally used. Steam ports are drilled in the press-platens and by using suitable baffles in the ports the steam is directed through the platen in a grid-iron path. The steam is led into the top platen first and then into the lower one: this reduces water-logging to a minimum. In direct mould heating the mould itself is channelled. The connexions to and from the moving platen obviously must be flexible. Knuckle-jointed pipes, reinforced rubber hose, drawn copper tubing with ridges, and copper spiral tubes are used for this purpose.

In order to obtain a platen temperature of 355-60° F. the supply boiler is run at 160-70 lb. per sq. in. gauge pressure and the steam admitted into the supply pipe through a reducing valve set at 150 lb. per sq. in.: the reducing valve delivers steam at a steady pressure although the boiler pressure may vary. In order to prevent water-logging and to conserve steam the waste steam from the platens is generally passed into a steam trap.

Hot-water heating. Hot water under pressure is sometimes used to heat presses. In this case water is taken from a Lancashire type boiler, but below the water-line, and circulated by pumps through the press platens and back to the boiler. The temperature of the water leaving the boiler is the same as that of the steam under pressure, above the water-line. An advantage of using hot water under pressure is that steam traps are not required.

Gas heating.⁴ With gas heating the moulds are generally heated by contact with hot platens, but in some cases gas jets are applied direct to the moulds. Platens for gas heating are designed with circular or rectangular channels in them for the insertion of gas bar-burners. These channels form the combustion chambers. Ordinary town gas at a pressure of about 4" water pressure is used, and the oxygen for combustion is drawn into the combustion chamber from the air. The chief difficulties with gas heating are (1) to get an adequate supply of air into the combustion chambers, (2) to remove the products of combustion, and (3) to overcome variations in platen temperature owing to variations in gas pressure. These difficulties are largely overcome if gas mixed with part of the air is supplied to the presses under high pressure from a compressor. The high jet velocity of the gas mixture draws in an adequate further supply of air and drives out the products of combustion. Alternatively, town gas can be used with bimetal thermostats. If the gas pressure falls the butterfly valve opens slightly to admit more gas.

Electric heating.⁵ Strip heaters or heating elements consist of

spirals of nickel-chromium wire embedded in a refractory material enclosed in a chromium steel sheath. The elements are fixed in appropriate slots in the platens. Each platen is connected up as a separate heating unit, the elements being connected in series and the temperature controlled by means of a thermostat. Heating elements can be applied direct to the mould.

Steam heating has the advantages of being cheap, of rapidly raising the platens to the desired temperature, of giving a steady platen temperature, and of being rapidly chilled by running cooling water through the platen in those cases where it is advantageous to chill the moulding before ejection.

Gas heating is generally rather more expensive to run than steam heating and it is not easy to maintain steady platen temperatures. It is considerably cheaper to install, since an expensive boiler, valves, and piping are not required. Gas-heated platens cannot be chilled, but they can be run at different temperatures, an expedient which is adopted sometimes to assist ejection, since the moulding sticks to the colder force of the mould.

Electric heating is more expensive still, but it is clean, as it avoids water-drips and gas fumes. It is rather slow in getting up to temperature, but temperature control is easy and steadier, and the platens can be run at different temperatures. Electrically heated platens cannot readily be chilled.

Hydraulic Pressure.

There are two industrial methods of applying hydraulic pressure to moulding presses.

In one system the press and pressure pumps make up a self-contained unit with a small special type of pump supplying a steady pressure for its own press. This system has its attractions, since it means that a press can be worked independently, as it is not dependent on the general supply for its hydraulic pressure.

Most moulding shops however work on the system of having a general supply of hydraulic pressure for all of the presses. Commonly the hydraulic pressure is obtained from a three or four throw ram pump (Fig. 31), which consists essentially of three or four pistons and cylinders delivering the water to the supply line. The water cannot be taken directly from the ram pump to the presses, since the pump delivers a pulsating pressure. The water delivered from the pump is led to an accumulator (Fig. 32), which generally consists of a large cylinder with a piston which supports a weight, the weight of the piston and its supported weight being enough to give a pressure of 1 ton per sq. in. on the piston face in contact with the water. The supply line to the presses is taken from the accumulator cylinder, so that a reasonably steady line pressure is obtained. Besides acting as a pressure stabilizer, the accumulator acts as a store for hydraulic pressure by reason of its cylinder capacity.

The accumulator is so designed that when the ram pump has filled

the cylinder and raised the accumulator ram to its maximum safe distance, the pump is cut out by a deflecting valve. When presses are opened to the supply line, water under pressure is drawn off from the

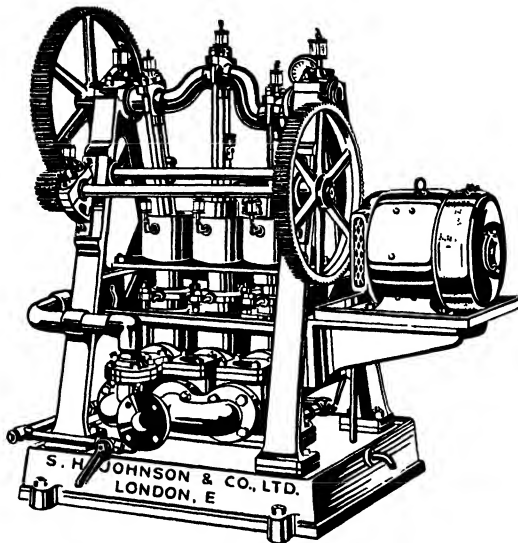


FIG. 31. Three-throw Ram Pump

accumulator cylinder and the ram falls; this automatically cuts the ram pump in. Various safety devices are incorporated to prevent mishaps. The ram pump and accumulator should be of such a size that they can together cope with the maximum volume requirements of high-pressure water, if all of the presses connected to the supply lines are opened to the pressure at the same time. This can be calculated from the rate of delivery of the pump, the capacity of the accumulator, the diameter and length of stroke of each press, and the speed of each press stroke.

An alternative form of accumulator is the air-loaded type. In this accumulator a cushion of compressed air takes the place of the heavy weight and no piston is required. The air accumulator has the advantage of requiring only light foundations.

Transfer Moulding.

Recently a kind of injection moulding has been applied to the thermo-setting moulding powders (phenolic and urea).

To distinguish it from *injection* moulding as applied to *thermo-plastics* proper it is generally known as *transfer* moulding. As will be seen later, there are several important differences between *injection* and *transfer* moulding, so the distinction is a good one.

In its simplest conception transfer moulding consists of the forcing

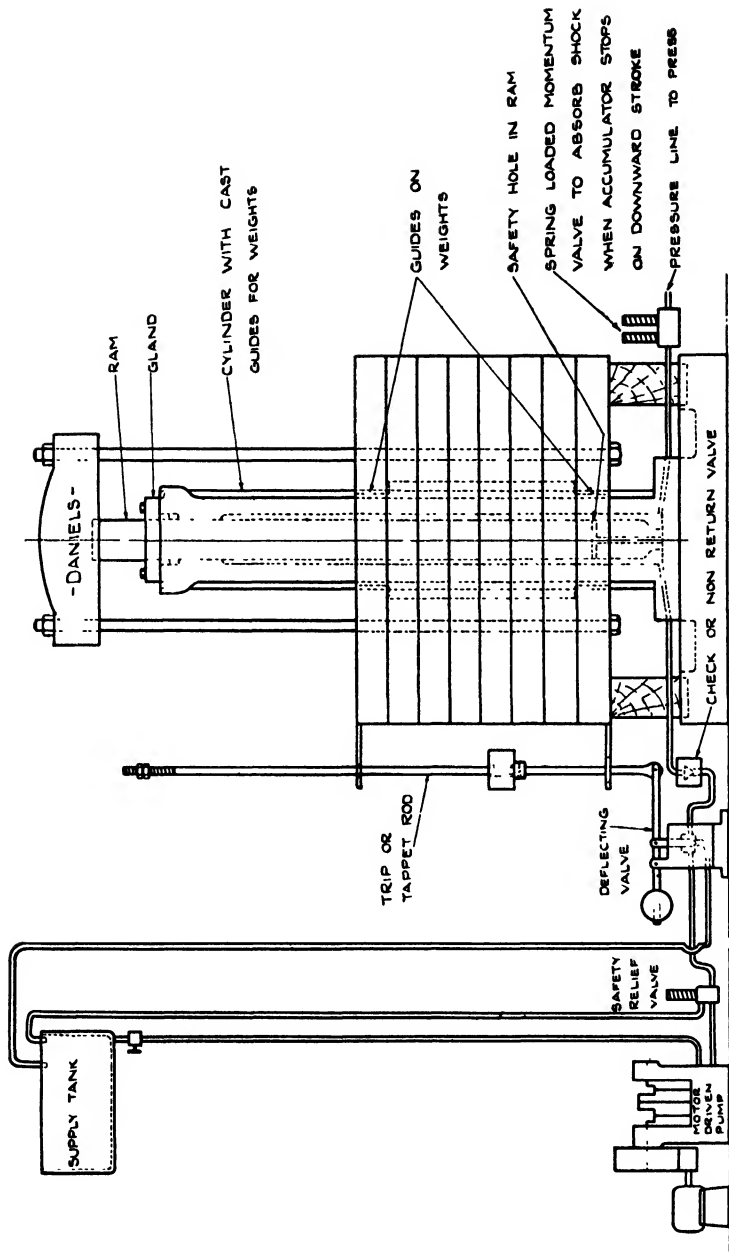


FIG. 32. Weight-loaded Accumulator System

by means of a hydraulic pressure-plunger of thermo-setting moulding material from a charging cavity through an orifice, called the gate or passage, into a hot moulding-cavity. According to the drawings

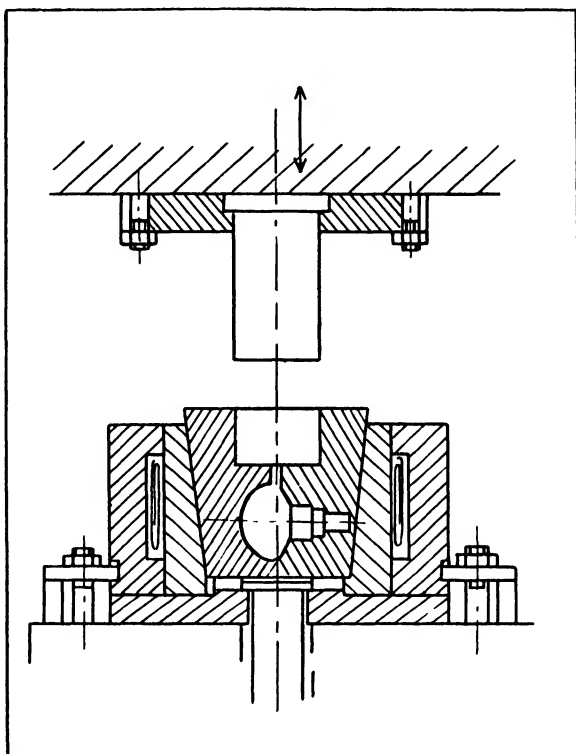


FIG. 33. Transfer Mould

given by Amigo,⁶ a typical transfer moulding set-up consists of a down-stroke press with a pressure ram fixed to the top platen. The mould is fixed to the bottom platen and consists of an outer casing carrying the heating elements. Inside the casing is a locking chase into which fits the split body of the mould. In the top of the split body is the loading chamber, into which operates the ram fixed to the top platen. Leading from the loading chamber is the gate or passage communicating with the mould cavity. A subsidiary up-stroke ejector ram operates through the bottom platen on to the base of the split body which is advantageously tapered. Provision must be made for the escape of air from the mould through the split or by means of special vents.

Ordinary thermo-setting moulding powders or pellets appear to be

used, although Shaw⁷ states that the powders must be suitably selected in order to obtain good results. Moulding temperatures rather lower than those for ordinary compression work are employed. The mould is heated to the required temperature, but the ram is kept cold. A definite amount of moulding material is put into the hot filling or loading chamber and the press carefully closed. The ram compresses the powder, which becomes a plastic mass under the influence of the heat and pressure and flows through the gate into the moulding cavity. The material in the gate, called the stalk or cull, hardens first and the ram can then be withdrawn since the hardened cull holds the pressure. Heating is continued without ram pressure until the moulding is completely hardened. The split body of the mould is ejected by the subsidiary ram, the mould split open, and the cull broken off. By tapering the gate towards the mould cavity the cull breaks readily near the moulded piece where the cull has its smallest cross-section.⁸ The chief industrial difficulties in transfer moulding are in finding methods for stripping the mould and ejecting. Multiple cavity moulds can be used. With portable moulds (i.e. not fixed in the press) more than one mould can be used with one ram, so that whilst one moulding is heat-hardening another can be filled and possibly another stripped for recharging. In many instances the shape of the moulding permits of the use of a vertically split mould, but other moulded shapes may require horizontal splitting with consequent modifications of mould design.

Comparison of injection and transfer moulding. In transfer moulding the material is curing the whole time it is in the loading chamber and mould cavity, so that enough moulding material for one shot only can be used at a time. This is a fundamental difference from injection moulding, in which the barrel of the press may hold enough thermoplastic material for several shots.

In transfer moulding the mould is kept hot in order to cure the material, whilst in injection moulding the mould is kept cold in order to set the material.

Advantages of transfer moulding. In *compression* moulding of thermo-setting materials the mould is wide open when moulding material is put in, and it is then closed under high pressure. The effect of this high pressure in conjunction with heat is to cause the material to flow violently inside the mould cavity, and the surge of plastic material can, under certain circumstances, damage any projecting pins or inserts. Careful mould design and the use of pre-forms can, however, minimize, but not prevent this surge. Also compression moulding demands that an excess of moulding material should be used, the surplus being extruded from the mould as flash. It is difficult to keep this flash thin, and as the mould gets older the flash produced gets thicker. This flash has to be removed by a finishing operation. It is estimated that the average cost of finishing is about two-thirds of the cost of moulding.

In *transfer* moulding there is no great surge of plastic material, as it is admitted into the moulding cavity in a gentle stream through

a narrow gate. This is an advantage when delicate inserts have to be put into a moulding.

There is no flash on a transfer moulding except for the slight fin which is produced along the join in the split mould, so that the only finishing problem is the removal of the stalk and the concealment of the stalk scar. By judicious mould design the stalk can generally be placed at a spot where the scar is not noticeable.

A particular advantage of transfer moulding is for the production of thick lumpy mouldings, for example a billiard ball, in which it is difficult by compression moulding to get to the centre of the moulding the heat necessary for curing. By transfer moulding hot plastic material which readily cures is forced into the cavity.

Delafield⁹ has pointed out that in injection moulding of thermoplastics the moulding is built up in the form of a laminated onion-skin structure, and hence has greater physical strength than a similar moulding obtained from the same material by compression moulding. It has not been recorded whether a transfer moulding also has this onion-skin structure or consists of a mass of compacted sausage-like material. The nature of thermo-setting materials when plastic would appear to support the sausage-like structure.

Extrusion of Thermo-setting Moulding Materials.⁹

This process was originally patented and developed by the German firm Ang. Nowack A.G. and taken up in this country by Messrs. Rockhard Resins, Ltd.

Phenolic and urea-moulding materials are used, but as far as phenolic materials are concerned a special easy flowing, more expensive type of resin is used. Apparently only wood-flour fillers are used since asbestos, mineral, and fabric fillers give a bad surface.

Essentially the process consists of the use of a pulsating ram or punch working in a barrel or die which has zones of heat. The zone nearest to the ram is cold and the three other zones are progressively hotter as they near the other end of the barrel. As the ram moves to and fro fresh material is let into the barrel and it is forced through the barrel to the far end, where there is a profile of the cross-section required in the extruded material which, by passing through the heat zones, has become thermo-set. A braking device is required to retard the rate of extrusion so that the material is held in the die until it is properly cured.

In Fig. 34 the details of the machine shown are: (1) the funnel which feeds the die with powder; (2) the die or barrel; (3) the heating jacket and (3A) the steam-heating tubes or electric elements for the three heat zones; (4) the cooling jacket with (4A) the cooling tubes; (5) the braking or retarding device with adjusting lever; (6) and (7) the guide for the hardened extruded material as it comes out of the orifice; and (8) the punch which forces the material through the barrel.

A machine of this type, made by Messrs. T. H. & J. Daniels, Ltd., is illustrated in Fig. 35.

In operation the ram of the press is driven forward by means of hydraulic pressure, at first low and then automatically high when it meets with resistance from material in the feeding-chamber part of

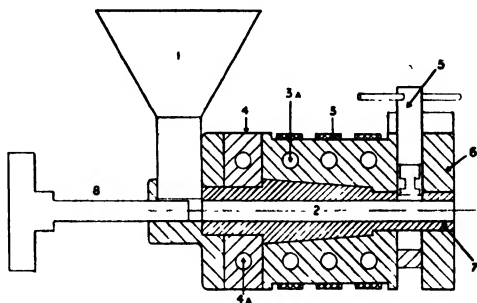


FIG. 34. Extrusion Moulding Machine

the barrel. Then the ram travels slowly, that is, at the rate of extrusion. At the end of its stroke the ram is automatically withdrawn by means of a powerful spring in order to admit more moulding powder. The powder in the barrel is kept practically in permanent motion, since the time-interval between the beginning of the back-stroke and the return-stroke is about 5 to 8 seconds. The pressure exerted by the ram varies from 250 lb. to $1\frac{1}{2}$ tons per sq. in., depending on the cross-section of the material extruded.

The first heat zone is kept between 50° and 80° , and in this zone the material is compacted and pre-warmed; this zone is slightly larger in cross-section than the extruding end of the press.

The second heat zone is kept at $130-50^{\circ}$, and here the powder begins to flux. The third heat zone is run at $175-90^{\circ}$ for phenolic

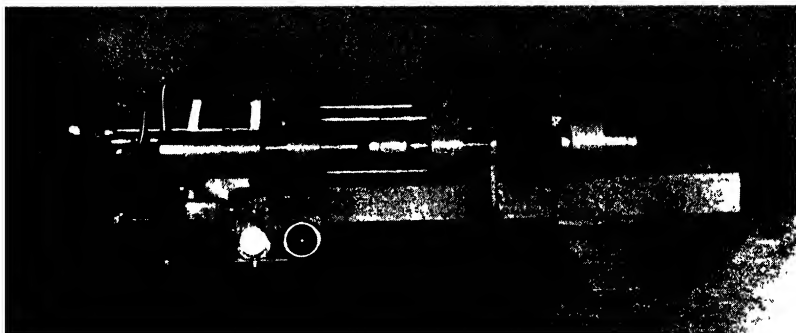


FIG. 35. Daniels' Extrusion Machine

powders or 165° for urea powders, and here the final shaping takes place, so it is essential that the cross-sectional dimensions should be absolutely accurate.

When starting up the machine the first few strokes merely compact the material and force it along the die at the outlet of which is placed a brass plug of the same cross-section as the extruding orifice. The first few inches extruded are crumbly and they eject the plug. When rigid material is obtained the braking device is applied, and after about 6 in. of material has been extruded, perfect

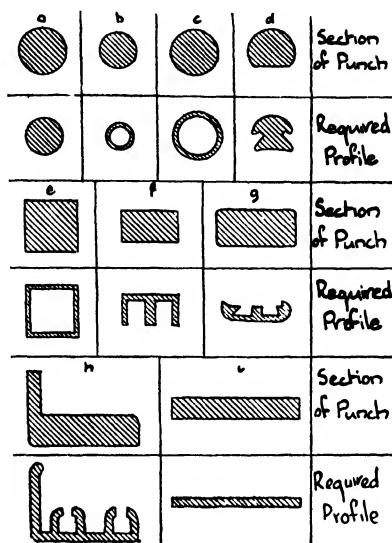


FIG. 36. Cross-section of Profiles

extrusion should be obtained. For a tube of $4\frac{1}{2}$ in. diameter the rate of extrusion is $4\frac{1}{2}$ –5 in. per minute and a 1 in. diameter tube at about 10 in. per minute. At the end of the day's run a non-hardening powder is fed in so that the machine is not 'bunged up', as would be the case if ordinary material were left in the barrel.

A variety of cross-sections or profiles can be extruded and it is customary to have the punch and barrel of cross-section modified to suit (Fig. 36). Different types of powder are required for the production of different profiles; for example, a powder satisfactory for a 1 in. diameter tube will not do for a $4\frac{1}{2}$ in. diameter tube.

This extrusion process is used for the production of beading, for window ledges, furniture, picture frames and panelling, for bathroom, railway carriage, motor-car, and ship's fittings, lamp standards, kettle holders, and Gestetner duplicating rolls. Boards of 4 to 5 in. wide have been produced, and it is visualized that wide boards could be obtained with large machines.

The properties of extruded thermo-setting plastics are the same as those of compression-moulded material except that the impact strength is about 50 per cent. higher, an improvement ascribed to the orientation necessarily obtained by an extrusion process.

Although it is claimed that absolutely smooth extrusion is obtained, in point of fact samples of extruded material which have been exhibited show on very close examination a series of very fine striations.

Cellulose acetate compositions can be extruded on this type of machine provided that there is a cold zone at the extruding end.

REFERENCES

1. *Br. Plastics*, 1939, 11, 121, 10.
2. C. A. Redfarn, *Br. Plastics*, 1940, 12, 135, 84, 85; B P. 481,763, 421,577, 485,392.
3. B P. 493,165.
4. Industrial Uses of Gas, No. 4; Br Commercial Gas Association.
5. Sanderson, *Br. Plastics Year Book*, 1933, 12.
6. A. Amigo, *Br. Plastics*, 1939, 10, 19, 629.
7. Shaw, *Modern Plastics*, 1939, 17, 2, 240.
8. G. K. Scribner, *Modern Plastics*, 1938, 16, 2, 23.
9. P. A. DeLafield, *Inst Plast. Ind. Trans.*, 1936, 92.

IV

TESTING OF PHENOLIC MATERIALS ACCORDING TO
B.S. SPECIFICATIONS**Testing of Phenolic Moulding Materials and Mouldings according to B.S.S., No. 771, 1938.**

Many methods of test, derived from rubber-testing and metal-testing methods, have, in the past, been applied to phenolic moulding materials and mouldings.

Within the last few years a British Standards Specification, No. 771, 1938, has been brought out specially for these phenolic materials. The tests given in the specification are briefly as follows:

A. Density. The moulded sample is weighed in air and again in water at 20°. The density in gm. per millilitre is given by

$$D = \frac{W_A}{W_A - W_W},$$

where D = density of sample in gm./ml. at 20°,

W_A = weight of sample in air,

W_W = weight of sample in water.

B. Acetone extract. A sample, obtained by sieving the filings from a moulding (using a specified file and sieve), is dried *in vacuo* and soxhlet-extracted with acetone. The difference in weight of the dry powder in the thimble before and after extraction is taken and the percentage acetone extract calculated. This value is a measure of the degree of cure of the moulding, since acetone extracts principally free phenol and low molecular weight phenol-formaldehyde condensates. It should not exceed 6 per cent.

C. Ultimate tensile strength. A dumb-bell specimen of definite dimensions (0.375 in. at thickest section) is moulded in a positive mould at 1–2 tons per sq. in. pressure, and 300–30° F. (149–65° C.) mould temperature. The moulding time is 15 minutes, and chilling before ejection may be employed.

Almost any standard tensile strength machine may be used, and the ultimate tensile strength is expressed in lb. per sq. in. on the original minimum cross-sectional area calculated from the measured dimensions of the specimen.

D. Impact strength. A notched test-piece of definite dimensions (2.5 in. × 0.5 in. × 0.5 in.) is moulded in a flash or positive mould at 1–2 tons per sq. in. pressure and 300–30° F. (149–65° C.) mould temperature for 15 minutes with chilling before ejection. The test-piece is mounted in an Izod-type impact testing machine and fractured under specified conditions. The impact strength is given in foot-pounds of energy absorbed in breaking the specimen.

E. Water absorption and swelling after immersion. A disc of specified dimensions is moulded in a positive mould at 1–2 tons per sq. in. pressure and 300–30° F. (149–65° C.) mould temperature for 15 minutes with chilling before ejection if necessary. The disc has the skin taken off and is smoothed to definite dimensions (1.89 in. diameter, 0.394 in. thick). After conditioning, the disc is measured and weighed, immersed in water for a week, dried with blotting-paper, and re-measured and re-weighed. The water absorption is expressed as the increase in weight in milligrammes on the test-piece. The swelling after immersion is given in inches. It is the average increase in thickness and diameter of the test-piece.

F. Plastic yield. A test-piece 200 mm. × 5 mm. × 5 mm., notched near one end, is machined out of a larger moulded piece or obtained by moulding to the finished dimensions.

The specimen is moulded in a positive mould at 1–2 tons per sq. in. pressure and 300–30° F. (149–65° C.) mould temperature for 15 minutes with chilling before ejection if necessary.

The specimen is then fixed in a clamp (see Fig. 6 in B.S.S. 771, 1938) in an oven maintained within 5° of a given temperature (100–80°) depending on the class of material being tested (see table on p. 164). A stirrup with pan weighing not more than 20 gm. is hung on the notch and after 15 minutes in the oven the height of the unsupported end of the test-piece is measured from a suitable datum line. The total load applied to the specimen by means of the stirrup is increased to 450 gm., and the conditions maintained for 6 hours. The height from the datum line is again measured and the difference between the two measurements in millimetres gives the plastic yield.

G. Electric strength. A disc 4–5 in. diameter, 0.125 in. thick is moulded in a flash or positive mould at 1–2 tons per sq. in. pressure and 300–30° F. (149–65° C.) mould temperature for 6 minutes with chilling before ejection if necessary. The sample is pressed between two brass electrodes, the lower one 3 in. diameter, 1 in. thick, and the upper one 1½ in. diameter, 1½ in. thick.

The sample is immersed in insulating oil and the electrodes and specimen maintained at 90° for 15–20 minutes. The test voltage specified for the type of material (20–60 volts per mil; see table, p. 164) is applied by means of an alternating voltage of 50 cycles per second, which is raised from zero to the full test value at a rate not less than 1 kV. per second and maintained there for 1 minute. No breakdown should occur.

H. Surface resistivity. A disc 4–5 in. diameter, 0.125 in. thick is moulded in a flash or positive mould at 1–2 tons per sq. in. pressure and 300–30° F. (149–65° C.) for 6 minutes with chilling before ejection if necessary. The specimen is immersed in water for 24 hours and dried with blotting-paper. In the test the specimen is placed horizontally and two electrodes applied. The electrodes consist of an inner disc of mercury 50 mm. in diameter, the mercury¹ being retained in position by means of a thin copper ring with knife-edge contacts, and an outer ring of mercury of 70 mm. smaller diameter and 80 mm. larger diameter, the mercury ring being kept in place by means of two copper rings with knife edges. The essence of the test consists of the measurement of the electrical resistance of the annular surface of the moulding between the inner mercury disc and the outer mercury ring. The test is carried out at a potential difference of 500 volts D.C., and calculated from the following formula:

Surface resistivity in megohms

$$\frac{2 \times \text{surface resistance of circuit in megohms}}{\log_e \frac{\text{longer diameter of annular surface}}{\text{shorter diameter of annular surface}}}$$

J. Resistance to crushing after heating. A cylinder 0.375 in. long \times 0.375 in. diameter is machined from a moulded piece, with the axis of the cylinder parallel to the moulding pressure. The specimen is heated in an air oven for 12 hours at 130–40° F., then 6 hours at 165–75° F., followed by heating for 30 minutes at 390–410° F. by means of total immersion in fusible metal. After cooling, a compressive load of 500 lb. is applied for 1 minute, and the specimen should not rupture. This test is applied only to heat-resistant (i.e. asbestos-filled) material.

K. Powder density and bulk factor. Under special conditions, the weight of 100 c.c. of loosely packed moulding powder is determined, and the apparent powder density expressed as the weight in gm. of 1 c.c. of the powder. The bulk factor is calculated by dividing the density of a moulded specimen obtained by the method outlined in section A, by the apparent powder density; thus the bulk factor is the number of times that the volume of the powder is greater than the volume of the finished moulding.

L. Flow by cup flow test. In the hot pressing of phenolic moulding powder two factors come into play: (1) the flow or

plasticity of the material which enables it to fill all of the parts of the mould; (2) the 'curing' of material so that it is set permanently to the shape of the mould.

It is difficult in practice to separate these two factors, but that they do exist can be readily deduced from the fact that two moulding powders of the same 'curing' time will not work in the same way in a given mould.

There are several methods of assessing the flowing properties of a phenolic moulding powder, but the only one with any official standing in this country is that known as the British Plastics Federation Cup Flow Test, described in B.S.S., No. 771, 1938.

The mould used produces a beaker with a base of varying thickness. The mould cavity is standard with regard to its height, diameter, taper, bottom thickness, thermometer hole position, and 'flash' construction.

The use of a portable mould is not now considered as standard; a mould, channelled for steam heating and fixed in a suitable press, is taken as standard in the event of dispute.

The moulding temperature used is $325^{\circ}\text{F.} \pm 2^{\circ}\text{F.}$ ($163^{\circ}\text{C.} \pm 1.1^{\circ}\text{C.}$) and the pressure 10 tons $\pm \frac{1}{2}$ ton (10160 kg. \pm 508 kg.) on the mould. An accumulator-fed line pressure is considered standard.

The weight of moulding powder taken should be enough to give a cup with a flash weighing not more than 3 gm. and not less than 2 gm.

The powder at room temperature $50\text{--}100^{\circ}\text{F.}$ ($10\text{--}37.8^{\circ}$) is put in the hot mould which is then closed; the time between putting the powder in and closing the mould should be between 5 and 10 seconds, and the press should be closed at a speed of 5 in. (127 mm.) in 4 to 5 seconds.

The time of flow is measured in seconds by means of a stop-watch, and is taken from the instant that the hydraulic gauge shows pressure to the instant that the flash ceases to move, the result being expressed as so many seconds 'Cup Flow'.

A soft, easy-flowing powder flows rapidly, so that the flash areas of the top and bottom faces of the mould are soon at their nearest distance to one another and no more material is extruded as flash. A stiff powder will, of course, require a longer time before the material extrudes to a sufficient extent to allow the flash areas to attain their minimum distance.

According to their cup flow times, phenolic moulding powders are graded as follows:

7-9	seconds	.	.	very soft.
10-12	"	.	.	soft.
13-17	"	.	.	medium.
18-22	"	.	.	stiff.
23-27	"	.	.	very stiff.

The Cup Flow test *seems to have given satisfaction in practice*, but has the appearance of having been improvised. For example, the top

outside diameter of the cup 2.450 in. \pm 0.001 in. and the overall height 2.342 in. \pm 0.001 in., although precise, are irritating to contemplate.

A further point is that the Cup Flow test measures neither the flow nor the curing time of a moulding powder. It does not measure the flow, since the flash ceases to move as soon as the flash areas reach the condition of minimum distance, although the powder may still have some flow left. It is, of course, possible that the measured amount of flow of two powders may be proportional to the total flow of the powders. The Cup Flow test is not a 'curing' time test, because, if the moulding is ejected as soon as the flash ceases to move, the moulding is usually blistered.

It has been stated that¹ in the Cup Flow test the mould is closed in 12 seconds (*sic*), but there are an enormous number of moulds in use in moulding shops which cannot be closed in so short a time. Under such conditions different powders with the same cup flow time can and do behave differently, dependent on their 'curing' times, a factor which is not measured by the Cup Flow test.

In actual moulding practice the 'curing' time is commonly taken as the time required to produce blister-proof mouldings in some particular mould available in the moulding shop.

There are many other methods for measuring the separate flow and 'curing' times, but none of them has official recognition in this country.

M. Shrinkage. The test specimen is a moulded disc 4.5 in. in diameter and 0.125 in. thick, moulded in a flash mould at 1-2 tons per sq. in. and at a mould temperature 310° F. \pm 2° F. (154.4° C.), for 6 minutes, ejected hot and allowed to cool in air. The difference between the diameter of cold mould and the cold moulding is divided by the diameter of the cold mould and expressed as thousandths of an inch per inch.

Types of material: the following types of material are dealt with in the specification:

G	General.
GX	Improved general.
MS	Medium shock-resistant.
HS	High shock-resistant.
HR	Heat-resistant.

The test values to which the different types should conform are given in the table on p. 164.

Discussion of Tests.

It will be observed that the tests on the finished mouldings are carried out on specially prepared mouldings made at rather lower temperatures and appreciably longer curing times than those generally employed in moulding shops. That is, care is taken—particularly in J—to ensure that as complete a cure as possible is obtained. This is different from moulding-shop practice, in which

Test	Section	Type				
		G	GX	MS	HS	HR
Ultimate tensile strength (lb. per sq. in.)	C	5,000	7,000	6,000	6,000	3,500
Impact strength (ft. lb.)	D	0-11	0-13	0-30	0-90	0-07
Water absorption (in gm.)	E	200	120	300	350	100
Swelling after immersion in water (in.)	F	0-003	0-003	0-006	0-010	0-002
Plastic yield	F	5 mm. at 100° C.	5 mm. at 140° C.	5 mm. at 100° C.	5 mm. at 100° C.	5 mm. at 180° C.
Electric strength at 90° C. (volts/mil)	G	20	60	20	20	20
Surface resistivity after immersion in water (megohms)	H	100	1,000	100	100	100
Resistance to crushing after heating (lb.)	J	500

Physical Properties

Impact strength, ft. lb. (B.S.S. 771)	0-17-0-22	0-17-0-22	0-17-0-22	0-16-0-20
Impact strength (cm. kg./sq. cm.)	1-4-1-6	1-4-1-6	1-4-1-6	1-4-1-6
Cross breaking strength (lb./sq. in.)	10,000-11,000	10,000-11,000	9,500-10,500	8,300-9,800
Tensile strength (lb./sq. in.)	6,500-7,500	6,500-7,500	6,000-7,000	5,500-6,500
Ultimate crushing stress (lb./sq. in.)	35,000-40,000	35,000-40,000	33,000-38,000	30,000-35,000
Brinell hardness (125 kg. on 5 mm. ball)	43-47	43-47	43-47	43-47
Specific gravity: Black	1-35	1-35	1-35	1-31
Brown	1-40	1-40	1-40	1-37
Weight per cub. in.	0-78 oz. 22-1 gm.	0-78 oz. 22-1 gm.	0-78 oz. 22-1 gm.	0-77 oz. 21-9 gm.
Modulus of elasticity in compression (lb./sq. in.)	6-2-7-2 × 10 ⁵	6-2-7-2 × 10 ⁵	6-2-7-2 × 10 ⁵	6-8-7-8 × 10 ⁵
Moisture absorption (24 hrs. immersion—specimen, 1½ in. × 1½ in. × ½ in.)	0-30-0-40%	0-32-0-42%	0-32-0-42%	0-40-0-50%

the curing time is very often cut down to the minimum required to give a moulding firm enough for ejection without distortion.

The test figures obtained in mouldings by the methods described in the specification represent, therefore, the optimum values obtainable, and should be regarded with reserve when computing the probable physical and electrical properties of mouldings produced under service conditions.

Power Factor (cf. Chapter XIV, p. 377).

The electrical tests for the power loss and power factor are becoming more and more recognized as the most important tests for evaluating the electrical properties of an insulating material.

Power loss and power factor are not dealt with in B.S.S. 771, 1938.

When an alternating potential is applied to a simple condenser consisting of two metal plates and a perfect dielectric (i.e. one in which no loss of electrical energy occurs), a charging current flows in and out of the plates without dissipation of energy. Energy is stored in the dielectric at increasing potential and delivered back to the circuit at decreasing potential, so that a wattmeter in the circuit would indicate no loss of power. In this case the current is 90° out of phase with the applied potential: if the same alternating potential were applied to a simple resistance the current would be exactly in phase.

With all practical dielectrics, however, the application of an alternating potential results in the loss of some power through the dissipation of electrical energy as heat, and a wattmeter in the circuit would indicate a power loss. When energy loss occurs in the dielectric the resulting current is a little less than 90° out of phase. This angle less than 90° is called the 'phase difference angle', and the difference between 90° and the phase difference angle is a small angle θ called the 'loss angle'. The size of the loss angle θ , which is the ratio of the power loss to the total power transmitted through the condenser, is defined as the power factor of the dielectric, the ratio usually being expressed as a percentage.

The argument can perhaps be made clearer by considering a diagrammatic layout [Figs. 37 (1), (2), and (3)].

(1) By this arrangement the power of the circuit is obtained in watts: let the value be represented by a .

(2) Now the power of the circuit will fall in comparison with (1), because all of the power absorbed by the insulator is not returned to the circuit, some of it being dissipated as heat. Let the value obtained from the wattmeter by this arrangement be represented by b . Hence $a-b$ gives the power loss.

(3) With this arrangement the power of the current transmitted by the insulator is obtained: let this value be represented by c .

The power factor of the insulator is given by $\frac{a-b}{c} \times 100$, that is,

$$\frac{\text{power loss}}{\text{power transmitted}} \times 100.$$

It must not for one moment be imagined that the layout on p. 166 is anything like the arrangement of the electrical equipment used in the determination of power factor, the layout merely being a hypothetical scheme devised to illustrate the principles involved.

With currents of increasing frequency the power loss increases rapidly, but the power factor generally decreases, indicating that at higher frequencies the amount of power transmitted increases at a greater rate than the increase in power loss. Since power loss is the result of dissipation of energy as heat, it follows that insulators with an appreciable power loss value become hot at high frequencies, the

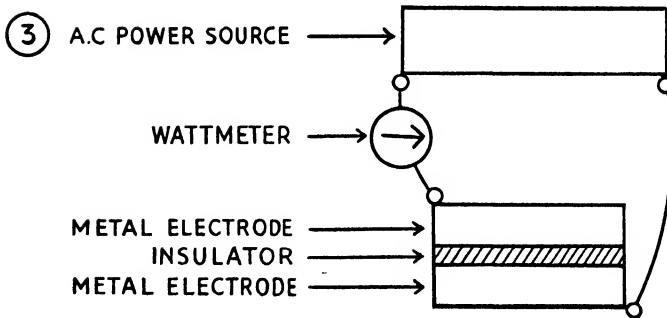
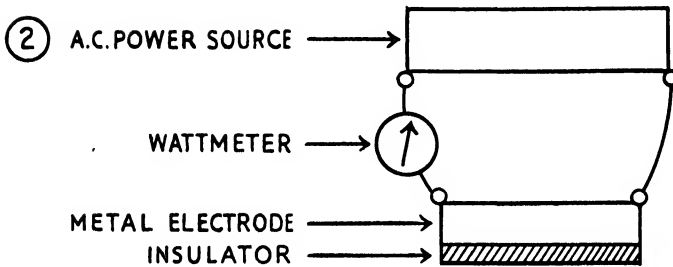
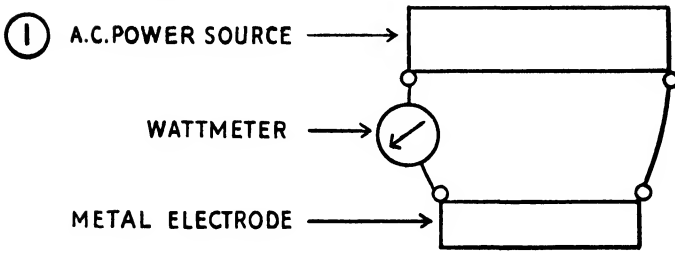


FIG. 37. Diagrammatic Power Factor Layout

heat impairing the insulating material and leading to the electrical breakdown of the insulator. In radio and television work where currents of high frequencies are used it is obvious that 'low loss'

material is desirable. Phenolic material, particularly that made specifically for the job by taking care to eliminate as far as possible water and other polar substances and taking precautions to cure the material thoroughly, has reasonably low power loss and power factor, e.g. 1.5-4 per cent. at 800 cycles. The synthetic plastic material with outstanding qualities with regard to power loss and power factor is polystyrene (q.v.).

Testing of Laminated Materials.

The testing of synthetic-resin varnish-paper boards and tubes (excluding tubes moulded after being rolled) for general electrical purposes is covered by B.S.S. No. 316, 1929, and high electrical paper material by B.S.S. No. 547, 1934. The material made with a fabric base and designed for use as a gear material is covered by B.S.S. No. 668, 1936.

Recently a War Emergency B.S.S. No. 971, 1941, for Synthetic Resin Bonded Fabric Sheet for Electrical and Mechanical Purposes has been published.

B.S.S. No. 316, 1929.

(1) **Definitions.** Synthetic-resin varnish-paper board (or tube) denotes a board (or tube) made from superimposed layers of paper treated with synthetic-resin varnish.

(2) **Grading.** *Grade I* material has the principal characteristics of low moisture absorption, high resistivity, low dielectric (power) loss at radio frequencies, and good machining properties. *Grade II* material has the principal characteristic of high electric strength at high temperature. It is the grade generally used on oil-immersed plant, where high electrical strength at high temperature is required, and on low-voltage apparatus in air. In general *Grade II* material has not as good machining properties as *Grade I*, but is less brittle.

(3) **Perpendicular.** The term 'perpendicular' denotes the direction normal to the surface of the material. A board is sometimes built up as superimposed layers with the grain at right angles.

(4) **Scope.** The specification deals only with *Grade II* material, *Grade I* material being covered by B.S.S. No. 547, 1934. Boards up to $\frac{1}{2}$ in. thick and tubes of wall thickness up to $\frac{1}{4}$ in. only are considered. Tubes of internal diameter greater than 3 in. are referred to as cylinders and not covered by the specification.

(5) **Finish.** Boards and tubes shall be uniformly and smoothly finished and free from splitting and excessive twisting. Tubes shall be finished all over with a protective coating of moisture-resisting insulating varnish. It is recommended that material for use in air should be dried out and all machined surfaces coated with the protective varnish.

Before carrying out tests the specimens are conditioned at 15-25° in an atmosphere of 75 per cent. relative humidity for at least 18 hours.

(6) **Tolerance of dimensions.** The measurements on boards and tubes are made with suitable micrometers. The dimensions, i.e. thickness of boards, wall thickness, internal and external diameters of tubes, shall not exceed limits given in tables for a range of thicknesses and diameters. Tubes of wall thickness greater than $\frac{1}{8}$ in. are tested for straightness.

(7) **Density.** The density is determined by weighing the sample in air and then in water or by direct measurement, calculating the volume and weighing. The density is expressed as gm. per c.c. and shall be not less than 1.30 for boards and 1.20 for tubes.

(8) **Insulation resistance.** For testing boards, two $\frac{1}{2}$ in. holes with an inch space between are fitted with brass stud electrodes, whilst for tubes an inch length of tube is held between two metal plate electrodes. By means of a D.C. voltage of about 500 the insulation resistance is measured at 90° in air. If the material is to be used in air, the test is repeated at 15–25° at 75 per cent. relative humidity.

The resistance in all cases shall not be less than 1,000 megohms.

(9) **Electric strength at 90° C.** The test specimen of board or tube is held between appropriate brass electrodes and immersed in transformer oil at 90°. The test is made with an alternating voltage of about 50 cycles per second, and the full voltage applied for 1 minute. For boards the test voltage which the sample must withstand ranges from 17½ to 50 kilovolts, over a thickness range of $\frac{1}{8}$ in. to $\frac{1}{2}$ in. For tubes the test voltage ranges from 250 to 200 volts per mil.

(10) **Surface breakdown in air.** Electrodes arranged as in section (8) are used and the test is carried out in air (15–25° and relative humidity 75 per cent). A 50-cycle A.C. test voltage of 14 kilovolts for boards or 12 kilovolts for tubes is applied for 1 minute. The difference in test voltages has been adopted owing to the better surface obtained in board manufacture.

(11) **Breakdown along laminae under oil.** A piece of board 1 in. × 2 in. is clamped between two metal electrodes, so that the two opposite edges of the specimen, 1 in. apart, are in contact with the electrode. With tubes a test-piece 1 in. long is used.

The electrodes and test-piece are immersed in transformer oil at 90° and a test voltage of 20 kilovolts (A.C. 50 cycles per second) applied for 1 minute. There should be no breakdown along the laminae of the sample.

(12) **Tensile strength of boards.** To a dumb-bell specimen of definite dimensions (the thickness being that of the board under test) the load is steadily increased at such a rate that the test-piece breaks in about 2 minutes. The tensile strength in either direction of a board shall be not less than 10,000 lb. per sq. in.

(13) **Compression strength.** For boards the test-piece is a 1 in. cube built up of several layers which are bedded together under a load of 300 lb. per sq. in. The length of the specimen in the direction of the pressure is measured at 300 lb. per sq. in. and the

load increased to 10,000 lb. per sq. in. The reduction in the measured length shall not exceed 3 per cent.

For tubes, the length of the specimen shall be equal to the external diameter of the tube and an initial load of 300 lb. per sq. in. is applied end on. The load is increased gradually at such a rate that the specimen crushes in about 2 minutes. The initial 300 lb. load is included when computing the load required to cause failure. The minimum ultimate compression strength ranges from 10,000 to 12,000 lb. per sq. in. over a range of wall thickness from $\frac{1}{8}$ in. to $\frac{1}{4}$ in.

(14) Shearing strength of boards. For boards up to $\frac{1}{2}$ in. thick the shearing strength is tested by determining the load required to punch a hole $\frac{1}{2}$ in. in diameter, the load being applied at a rate of approximately 100 lb. per minute for each $\frac{1}{32}$ in. thickness of the specimen.

For boards above $\frac{1}{8}$ in. thick a specimen 5 in. long by $2\frac{1}{2}$ in. wide is clamped in a special jig, so that a test surface $2\frac{1}{2}$ in. \times 2 in. is exposed. A plunger with surface 2 in. wide \times 7 in. long running on side guide-pins is applied to the exposed surface of the test-piece and the load applied. The stress shear is calculated on the total area of the sections sheared off. The shear stress expressed in lb. per sq. in. of the sheared area shall not be less than 11,000 lb. per sq. in.

(15) Cohesion between layers. For boards, a specimen 1 in. wide and of length equal to $\frac{1}{2}$ in. plus four times the thickness of the board is supported on vee-blocks spaced apart at a distance equal to four times the thickness of the board. The specimen is placed so that the laminations are horizontal. By means of a wedge-shaped plunger $1\frac{1}{2}$ in. wide at the top with a wedge angle of 45° and the pressure edge rounded off, the load is gradually applied to the centre of the specimen and maintained for 1 minute. The specimens are cut in either direction and the test load ranges from 150 lb. to 1,100 lb. over a range of thickness from $\frac{1}{16}$ in. to $\frac{1}{2}$ in. The specimen under the appropriate load for 1 minute should show no signs of splitting or other failure.

For tubes a specimen of length equal to the external diameter is submitted to an end-on compression load which is maintained for 1 minute, and no signs of splitting or other failure should appear. The test load ranges from 200 to 400 lb. over a range of $\frac{1}{8}$ in. to $\frac{1}{4}$ in. wall thickness.

(16) Water absorption. For boards a specimen $1\frac{1}{2}$ in. \times $1\frac{1}{2}$ in. is weighed before and after 24 hours' immersion in water, and the percentage increase in weight should not be more than the appropriate value, which ranges from 4 to 1 per cent. over a range of $\frac{1}{16}$ in. to $\frac{1}{2}$ in. thickness.

For tubes, a $1\frac{1}{2}$ in. length is taken, and the percentage increase in weight should not exceed the appropriate value, which ranges from 6 to 3 per cent. over a wall thickness of $\frac{1}{8}$ in. to $\frac{1}{4}$ in.

(17) Effect of hot oil. A specimen of board 3 in. square or tube 3 in. long is immersed in transformer oil at $110\text{--}15^\circ$ for 24 hours

and should then show no appreciable signs of warping, splitting, blistering, disintegration, or other deterioration.

(18) **Softening-point of boards.** A method of test has not yet been adopted.

(19) **Machining tests.** Boards shall be capable of being sawn, milled, drilled, and tapped with a No. 0 B.A. tap and shaped in a shaping machine without showing signs of splitting, cracking, or chipping. Boards up to $\frac{1}{16}$ in. thick shall be capable of being punched.

Tubes shall be capable of being sawn, drilled, and tapped with a No. 0 B.A. tap without splitting, cracking, or chipping.

(20) **Freedom from chemical impurities.** A method of test has not yet been adopted.

(21) **Corrosion of metal inserts.** The specification states that boards and tubes shall not cause corrosion to metal in intimate contact with the material, but no further details are given.

B.S.S. No. 547, 1934.

(1) **Scope.** The specification covers Grade I material up to $\frac{1}{2}$ in. thick, but does not cover rods or tubes. For thicknesses below $\frac{1}{8}$ in. two classes of material are recognized, ordinary class, and punching class.

(2) **Definitions.** The term 'synthetic resin bonded paper sheet' denotes a sheet, board, plate, or panel made from paper or pulp treated with synthetic resin and bonded under heat and pressure.

(3) **Grade I material.** Grade I material is distinguished from Grade II material by its low water absorption, high resistivity, low dielectric loss, and good machining properties. Grade I material is generally used in apparatus working under humid conditions. Grade II material is generally used in oil-immersed apparatus and in low-voltage apparatus working in dry air.

Generally it is not necessary to protect the surfaces and edges of Grade I material with moisture-resisting insulating varnish, although this may be desirable in certain circumstances. Such protection is generally necessary with Grade II material when it is used in air.

Before carrying out tests the specimens are conditioned at 15–25° in an atmosphere of 75 per cent. relative humidity for at least 18 hours, except in the case of the test described under (7).

(4) **Finish.** Sheets shall be smoothly finished and free from detrimental local deformation, splitting, and excessive twisting. They are tested for flatness with a straight edge and should not be more than $\frac{1}{4}$ in. out on a length of 36 in.

(5) **Tolerance in dimensions.** The permissible variation in the thickness of the sheets from the nominal thickness is given in a table. The thickness is measured by means of a suitable micrometer on the sheet as received (i.e. no conditioning).

(6) **Density.** The density of the sheets covered by this specification is approximately 1.38 gm. per c.c.: density is no guide to the quality of a sheet.

(7) **Insulation resistance.** The test specimen 6 in. \times 1 $\frac{1}{4}$ in. is cleaned with benzene before testing. Electrodes of graphite are used and they are formed by applying with a brush a colloidal suspension of graphite in water of the kind sold commercially for lubricating purposes. Two films of graphite $\frac{1}{4}$ in. wide \times 4 in. long with a $\frac{1}{4}$ in. space between them are applied symmetrically to one face of the specimen and a similar pair applied to the other opposite face. The specimen is then submitted to a controlled atmosphere of 90 per cent. relative humidity at 50° for 24 hours. The insulation resistance is measured at 500 volts between the two pairs of electrodes, each pair being connected in parallel, whilst the specimen is in the controlled atmosphere. The reading is taken after 1 minute's electrification and shall be not less than 1,000 megohms.

(8) **Electrical strength at 90°.** The specimen is held between two brass electrodes, the upper one being a cylinder 1 $\frac{1}{2}$ in. diameter and 1 $\frac{1}{2}$ in. high, and the lower one a block 3 in. diameter and 1 in. thick. The test is carried out in oil at 90° after the specimen and electrodes have been in the hot oil for $\frac{1}{2}$ hour. The test is made with an alternating voltage of about 50 cycles, and the specified test voltage is applied between the electrodes, one-third of it being applied at once and the rest at a rate of 1 kV. per second. The specimen shall withstand the test voltage for 1 minute without failure, the specified voltage ranging from about 17 to 40 kilovolts over a range thickness of $\frac{1}{16}$ in. to $\frac{1}{4}$ in.

(9) **Surface breakdown in air, after immersion in water.** The specimen, 6 in. \times 4 in., is immersed in water at 20° for 18 hours and wiped dry. It is then supported on an insulating block and two brass electrodes (cylinders 1 $\frac{1}{2}$ in. long, 1 $\frac{1}{2}$ in. diameter) placed on the top surface of the specimen with a distance of 1 in. between the electrodes. The test is made with an alternating voltage of about 50 cycles: one-third of the test voltage is applied at once and the rest at a rate of 1 kV. per second. The specimen shall withstand the test voltage for 1 minute without failure, the specified voltage being 10 kilovolts for thicknesses up to $\frac{1}{32}$ in. and 14 kilovolts for thicknesses from $\frac{1}{32}$ in. to $\frac{1}{2}$ in.

(10) **Breakdown along laminae in oil.** A specimen 1 in. \times 4 in. is held between two parallel metal plate electrodes so that the two opposite edges of the specimen 1 in. apart are in contact with the electrodes. After the specimen and electrodes have been in oil at 90° for $\frac{1}{2}$ hour an alternating voltage of about 50 cycles is applied, one-third of the test voltage being applied at once and the rest at a rate of 1 kV. per second. The specimen shall withstand the test voltage of 25 kilovolts for 1 minute without failure.

(11) **Tensile strength.** To a dumb-bell specimen of definite dimensions (the thickness being that of the sheet under test) the load is steadily increased at such a rate that the test-piece breaks in about 2 minutes. The tensile strength in either direction of a sheet shall not be less than 8,000 lb. per sq. in. Since a sheet may be built up of superimposed layers with the grain in adjacent sheets

at right angles, the term 'in either direction' may have no significance.

(12) Compressive strength. A test-piece, 1 in. cube, is built up of several layers of sheet and bedded together under a load of 300 lb. per sq. in. applied perpendicularly to the surface and the first measurement taken. A total load of 10,000 lb. per sq. in. is applied in the course of 2 minutes, maintained for 1 minute, and the yield measured. The reduction in length of the specimen shall not exceed 3 per cent. nor shall failure occur.

(13) Shearing strength. For sheets less than $\frac{1}{8}$ in. thick the shearing strength is tested by determining the load required to punch a hole $\frac{1}{2}$ in. diameter, the load being steadily applied at a rate of 100 lb. per minute for each $\frac{1}{32}$ in. thickness. The minimum shearing strength allowed ranges from 8,000 to 10,000 lb. per sq. in. of sheared-off area over a range of thickness from $\frac{1}{64}$ in. to $\frac{1}{16}$ in. The sheared-off area is the internal surface area of the hole produced.

For sheets of $\frac{1}{8}$ in. thick and over, the test-piece, $2\frac{1}{2}$ in. wide \times 5 in. long, is clamped in a shear-testing machine with a special jig so that a test surface $2\frac{1}{2}$ in. \times 2 in. is exposed. A plunger with surface 2 in. wide \times 7 in. long running on side guide-pins is applied to the exposed surface of the test-piece and the load applied so that both ends are sheared off simultaneously. The shear stress is calculated on the total area of the sections sheared off and shall be not less than 11,000 lb. per sq. in. in either direction. Since the grain in adjacent layers of the sheet may be at right angles, the term 'in either direction' may have no significance.

(14) Cohesion between layers for ordinary-class material. The test for cohesion between layers is applied by the bending method with ordinary-class material only. A specimen 1 in. wide and of length $\frac{1}{2}$ in. plus four times its thickness is supported on vee-blocks spaced apart at a distance equal to four times the thickness of the sheet. The specimen is placed so that the laminations are horizontal. By means of a plunger $1\frac{1}{2}$ in. wide with the bottom edge rounded the load is gradually applied to the centre of the specimen and maintained for 1 minute. The test is applied to specimens cut in either direction, and the test load ranges from 185 to 1,375 lb. over a range of thickness from $\frac{1}{16}$ in. to $\frac{1}{2}$ in.

The specimens shall show no signs of splitting along the laminae or other failure.

(15) Wrapping test for punching-class material. This test is applied to punching-class material up to $\frac{1}{8}$ in. thick only. The sheets shall be capable of being bent 180° round a rod of diameter equal to 90 times the thickness of the specimen without cracking or splitting along the laminae.

(16) Water absorption. A freshly cut specimen $1\frac{1}{2}$ in. square is weighed before and after 24 hours' immersion in water, and the percentage increase in weight shall not be more than the appropriate values. For Grade 1 (ordinary-class) material the value ranges from

approximately 1.6 to 0.1 per cent. over a range of thickness from $\frac{1}{100}$ in. to $\frac{1}{2}$ in. For Grade I (punching class) material the value ranges from approximately 4.5 to 0.9 per cent. over a range of thickness from $\frac{1}{48}$ in. to $\frac{1}{8}$ in.

(17) **Effect of hot oil.** A specimen approximately 3 in. square is immersed in oil for 24 hours at 110–15° and shall show no appreciable sign of warping, splitting, blistering, disintegration, or other deterioration.

(18) **Machining tests.** Sheets shall be capable of being sawn, milled, drilled, and tapped with a No. 0 B.A. tap and shaped in a shaping machine without showing signs of splitting, cracking, or chipping.

(19) **Punching test.** This test is applied to punching-class material only. The sheets shall be capable of being punched without signs of splitting, cracking, or chipping when the shortest distance between the hole and the edge of the sample is equal to the thickness of the sheet.

(20) **Impact test.** A method of test has not yet been adopted.

(21) **Softening-point.** A method of test has not yet been adopted.

(22) **Corrosion of metal inserts.** The specification states that sheets shall not cause corrosion to metal in intimate contact with the material, but no further details are given.

B.S.S. No. 668, 1936.

(1) **Scope.** The specification covers one grade of laminated synthetic resin bonded sheet from $\frac{1}{2}$ in. to 4 in. thick having medium to high mechanical strength and wearing properties, good machining properties, low moisture and oil absorption with consequent small tendency to swell. An added advantage is silent running when gear-wheels of the material are meshed with metal gears. The material is suitable for the production by the usual methods of high-class gears having teeth 16 D.P. or larger.

(2) **Definitions.** (a) Laminated Synthetic Resin Bonded Sheet (Fabric Base) for use as Gear Material denotes a sheet, board, or block of material made by superimposing layers of fabric treated with synthetic resin and hot-pressing them until solidified and cured to a permanently infusible state.

(b) Synthetic resin denotes a synthetic thermo-setting resinoid which becomes, when properly cured, hard, infusible, and insoluble in water.

(c) A gear blank is a square or circle sawn from sheet.

(d) Tested flatwise means that the load is applied perpendicularly to the plane of laminations.

(e) Tested edgewise means that the load is applied parallel to the plane of laminations.

(f) Tested lengthwise means that the specimen is cut and tested in the warp direction of the sheet.

(g) Tested crosswise means that the test specimen is cut and tested in the weft direction of the sheet.

The standard practice is to cut a circular blank out of sheet material and to cut teeth on its edge. Hence tensile strength tests are carried out lengthwise and crosswise, whilst compression and cross-breaking tests are carried out edgewise. Moulded gear blanks from fabric-filled moulding materials are not covered by this specification.

(3) **Finish.** The surface shall be uniformly smooth and flat within prescribed limits.

(4) **Tolerance of dimensions.** The thickness of the sheets is measured with a suitable micrometer and a plus tolerance only is allowed, ranging from 0.050 in. to 0.140 in. on a range of thicknesses from $\frac{1}{2}$ in. to 4 in.

(5) **Density.** The specific gravity of the material covered by the specifications is usually 1.32 to 1.38, about 20 cub. in. per pound.

(6) **Tensile strength.** A dumb-bell specimen of definite dimensions is machined out of a blank, the breaking part being $\frac{3}{4}$ in. to 1 in. by $\frac{3}{8}$ in. to $\frac{1}{2}$ in. cross-section. The test load is applied at a rate so that the breaking load is reached in 2 minutes. Four lengthwise and four crosswise specimens are tested and each four averaged. Whichever average is lower is taken as the value and expressed as lb. per sq. in.; the value shall not be less than 8,500 lb. per sq. in.

(7) **Resistance to compression.** The test-piece is a 1 in. cube cut from a sheet; sheets of less than 1 in. thickness are not tested for compression. The specimen is tested edgewise by applying a bedding load of 300 lb. measuring the length of the specimen in the direction of the pressure, and applying a proof load of 10,000 lb. during $\frac{1}{2}$ -1 minute. After 1 minute the test-piece is remeasured under load and the reduction in length shall not be more than 4 per cent. The specimen shall not show signs of splits, cracks, or delamination.

(8) **Toughness.** A method of test has not yet been adopted.

(9) **Cross-breaking strength.** Four test-pieces $\frac{1}{2}$ in. \times $\frac{1}{2}$ in. \times 6 in. are cut and tested lengthwise and four cut and tested crosswise. Under test the specimen is supported at two places 4 in. apart and the load applied on the opposite face midway between the supports. The load is applied so that the fracture takes place in about 2 minutes, and the modulus of rupture (*f*) calculated from

$$= \frac{3}{2} \times \frac{\text{breaking load (lb.)} \times \text{length between supports (in.)}}{\text{breadth (in.)} \times \text{depth}^2 \text{ (in.)}}$$

The lengthwise and crosswise results are averaged separately, and the lower average taken as the value which shall be not less than 16,000 lb. per sq. in.

(10) **Machining test.** The sheet shall be capable of being milled, drilled, and tapped with a No. 0 B.A. tap and shaped in a shaping machine without signs of splitting, cracking, or chipping.

(11) **Water absorption.** The specification covers sheets of not

less than $\frac{3}{4}$ in. thick. The test-piece used is $1\frac{1}{2}$ in. \times $1\frac{1}{2}$ in. on the face and $\frac{1}{2}$ in. thick. After conditioning the test-piece is weighed before and after 24 hours' immersion in water and the percentage increase shall not exceed 0.60 per cent.

(12) Effect of hot oil. The specification covers sheets of not less than 1 in. thick. The test-piece is a machined-out disc 6 in. in diameter and $\frac{3}{4}$ in. thick with a central hole 1 in. in diameter. The diameter of the test-piece is measured in four directions with a micrometer calliper and immersed in a specified type of mineral oil at 95–100° for 72 hours. On cooling and wiping free from oil the diameter is remeasured and the average increase in diameter shall not exceed 0.10 per cent.

REFERENCE

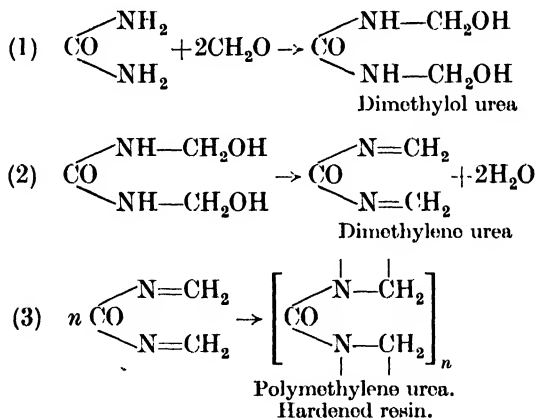
1. *Br. Plastics*, 1935, 6, 72, 547.

CHAPTER IV
UREA-FORMALDEHYDE RESINS

By C. A. REDFAEN

THE earliest work on the preparation of urea-formaldehyde resins was carried out by John,¹ who merely boiled urea and formalin together without a catalyst, and Goldschmidt and Neuss,² who carried out the reaction in the presence of small amounts of acids and acid salts. It was not, however, until Pollak and his collaborators worked on the problem that something of the nature of the reaction was understood and systematic industrial development work carried out.

Ideally, the reaction between urea and formaldehyde may be considered to take place in three stages:



By carrying the reaction out in the cold with a small amount of alkali present the process goes more or less completely to, and stops at, the dimethylol urea stage. Starting with urea, formaldehyde, and an acid catalyst, side reactions take place giving rise to insoluble products known as Goldschmidt's compounds,³ which are not resinous, do not flow under heat and pressure, and readily give off volatile matters when heated with acid. The successful production of urea-formaldehyde resins suitable for plastic materials depends on the prevention of the formation of these side reaction products.

Under acid conditions, preferably at elevated temperatures, dimethylol urea reacts in the direction of dimethylene urea, *but it is doubtful whether dimethylene urea ever exists as such in the reaction liquor*, since a methylene group, as soon as formed, probably polymerizes with another methylene group. The reaction to give methylene groups does not go to completion, and it may be taken

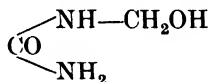
that there are still some methylol groups and possibly methylene groups remaining in thermo-hardened urea-formaldehyde resin.

The structure of thermo-hardened urea-formaldehyde resin is by general consensus of opinion considered to consist essentially of some form of dimethylene urea polymer, but nothing really definite is known of the chemical structure of the polymer, although E. B. de Chesne⁴ and G. Walter⁵ have propounded interesting theories.

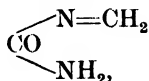
From the functionality point of view, the system urea:formaldehyde at first sight seems to be a 2:2 system, that is, if each —NH_2 is considered to have a reactivity of one, and formaldehyde reacting as methylene glycol $\text{CH}_2(\text{OH})_2$ to have a reactivity of two. However, the resin precursor may be considered to be dimethylene urea with two double bonds, each with a reactivity of two. The molecule is tetra-functional and so would be expected to give a thermo-hardened product.

As will have been observed, the theoretical amounts of urea and formaldehyde required are one molecular proportion of urea to two molecular proportions of formaldehyde. In practice, however, these proportions give a product which is apt to liberate formaldehyde during the thermo-setting process, giving rise to gassing and blistering troubles.

In consequence, a urea : formaldehyde ratio of 1 : 1.5 to 1.8 is used. This ratio necessitates that some of the urea combines with only enough formaldehyde to give monomethylol urea



and hence to monomethylene urea



a compound which has a reactivity of only two, so is non-thermo-setting.

From functionality considerations it will be readily recognized that this compound can form chain compounds only, but it merely requires to have an occasional dimethylene urea in the chain for cross-linking (thermo-setting) to take place.

It follows, therefore, that this reduction of the amount of formaldehyde in the urea-formaldehyde reaction will have the effect of overcoming the tendency to liberate formaldehyde but will not appreciably affect the thermo-hardening properties.

It has also been found that a urea-formaldehyde ratio of 1:1.5 gives a resin with the minimum water absorption.⁶ A ratio of 1:1.5 to 1.8 has been found to give a more rapidly thermo-setting product than that obtained with higher formaldehyde ratios.

The industrial development of urea-formaldehyde resins gained prominence from the work of Fritz Pollak in Vienna. In a series

of patents⁷ dating from 1920 the methods for preparing his materials known as 'Pollopas' are gradually developed, and as the patents proceed it is evident that the nature of the reaction between urea and formaldehyde is more clearly understood. From the beginning Pollak seems to have realized the importance of carrying out the first stage of the reaction in an alkaline medium, and eventually he was led to a two-stage process in which the second hardening stage is carried out under acid conditions. At first he was apparently more concerned with the production of a urea-formaldehyde syrup suitable for casting and baking to give a tough, hard, transparent product termed 'organic glass'. In brief, his process appears to consist of the reaction of urea and formaldehyde 'at the boil' with ammonia as catalyst followed by vacuum distillation under conditions of controlled acidity, the liquor being made acid before or during distillation. Glycerine may be added as plasticizer, and low-boiling solvents, which form constant boiling mixtures with water, may be added to facilitate removal of the water by distillation. At the end of the distillation the syrup is cast in glass or lead moulds and baked for several days at first at 60°, rising to 90° until the castings are hard and tough. During this hardening process it is difficult to avoid the formation of bubbles and fissures, and it was apparently this which led to the discarding of the urea-formaldehyde organic glass project and the adaptation of the process for the production of moulding powders. Various expedients for producing moulding powders are described in the Pollak patents, but no precise information is available as to the methods employed commercially for the manufacture of Pollopas moulding powder.

At about the same time that Pollopas was being developed, British Cyanides, Ltd. developed a process for the production of moulding powders from thio-urea $\text{CS}(\text{NH}_2)_2$ and formaldehyde. This was marketed by Beetle Products, Ltd., who at a later date acquired the Pollopas patents. Recently, British Cyanides, Ltd., changed their name to British Industrial Plastics, Ltd.

Moulding powders made from thio-urea are, owing to the presence of combined sulphur, apt to stain ordinary steel moulds, so that plated moulds have to be used. Moulding powders made by the Pollopas process require rather more care in moulding. For these reasons, the original Beetle powder and Pollopas, although still manufactured, are not used to any great extent.

It has recently transpired, through litigation, that the process employed in the manufacture of Beetle moulding powder is substantially that described in the B.P. 449,201 (now void). According to the patent, urea-formaldehyde moulding powders tend to lose their flowing properties during storage owing to premature curing of the potentially reactive resin, and that the process described overcomes this trouble. The first stage of the reaction between urea and formaldehyde, in the molecular proportions of about 1:1.5, is carried out in the cold under alkaline conditions, and when cellulose fillers are incorporated with this alkaline resin it has been found

possible to dry the charge in 8 hours at 90° without causing the resin to react to the hardened condition. In the example given in the patent, 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. After stirring for 2 hours the small amount of indigenous acidity is entirely neutralized. One part of 0.880 ammonia and 22 parts of technical urea are added and the temperature allowed to reach only 20°. Apparently in the course of 2 hours the temperature reaches 35° and then the syrup is ready for mixing with the filler.

Then 10 parts of the syrup are mixed at 40–50° for $\frac{1}{2}$ 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 $\frac{1}{2}$ per cent. of mould lubricant and $\frac{1}{2}$ per cent. of a plasticizer; next, the powder is ground with 1 per cent. of cinnamic acid. When wood-flour is used as filler, the proportions used are 2 resin syrup to 1 of filler, and the mixing carried out without heat.

Apparently cinnamic acid was chosen, since it is a sparingly water-soluble acid with m.p. 133°. This would mean that under moulding conditions at about 135° the acid is fluxed into the resin and is thus in a position to catalyse the hardening reaction.

The resin in the moulding powder contains combined water. If a water-soluble acid is ground in as catalyst the resin would dissolve the acid and bring about a slow hardening reaction known as cold cure, so that on storage the powder would lose its flow.

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. In the course of litigation it transpired that cinnamic acid is not used commercially, the nature of the accelerator not being disclosed. An inert substance which is apparently used is hexamethylene tetramine thio-cyanate (B.P. 351,093), a compound which decomposes and liberates acid at moulding temperatures.

In a patent⁸ which apparently deals with American modification of the process, further details are given; the lubricant is given as zinc stearate and after the final ball-milling the powder is sieved through muslin.

Another variation⁹ of the method of manufacturing urea-formaldehyde moulding powders is as follows:

Urea and formaldehyde are condensed by heating for 2½ to 3½ hours at pH 7.5–8, and incorporated with paper pulp in the ratio 306 parts of aqueous resin syrup to 174 parts of paper pulp. The mass obtained is dried in a rotary drier to 1–2 per cent. free moisture and ground with 0.2 per cent. zinc stearate, 0.1 per cent. cyclohexanol stearate (lubricants), and 1.0 per cent. tri-ethyl phosphate as hardening catalyst. Other hardening catalysts listed are dimethyl-ethyl-phosphate, tri-cresyl phosphate, and tri-methyl phosphate

The addition of 1 per cent. ammonium carbonate is recommended as stabilizer. It is stated that moulding powders made in this way can be stored for 6 months at 35° without deterioration. The interesting point about this process is the use of organic phosphates as hardening agents. Presumably, under moulding conditions free acidity is developed from the phosphates.

In a still more recent process¹⁰ urea and formalin in the molecular ratios 1:1.5 (21 parts urea : 40 parts formalin) are heated to 80° 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 and the liquor vacuum distilled until half of the water is removed: the pH value of the liquor is 8. The liquor is mixed with 16 parts wood-flour, lubricants, plasticizers, and colouring materials, and dried in a vacuum drier at 70°. After drying the material is treated on hot rollers in order to adjust the plasticity of the material. The sheets obtained are disintegrated to give moulding powder. Apparently under moulding conditions the hydrochloride salts of the nitrogen base used as catalyst for the first stage liberate acid to catalyse the hardening action.

Recent patents taken out by the Plaskon Company¹¹ state that substantial reduction in curing time of urea-formaldehyde moulding powders can be obtained by using 'latent' accelerators which generate weak organic acids during moulding. The list of accelerators includes acetoxime benzoate, acetoxime *p*-toluene sulphonate, ethylene thiocyanate, δ -gluconolactate, δ -galactonolactone, benzoate of benzhydroxamic acid, methyl saccharin, and cyano thio-formamide.

In March 1942, a series of six related patents¹² was published dealing with a development in urea-formaldehyde moulding powder manufacture which appears to be a distinct advance. The preamble common to all of the patents states that hitherto it has been the practice in urea-formaldehyde technique to convert the resin into the insoluble infusible condition by the late incorporation of a latent or directly active curing catalyst. This is not completely satisfactory since moulded articles produced from this admixed-catalyst type of composition often show blisters or discolorations. These defects are usually due to localized curing. In spite of the most careful precautions, there is considerable variation in the curing rates of individual batches, and even different portions of the same batch commonly show variations.

Since the value of moulded articles, specially light coloured ones, depends largely on appearance, the discovery of a means of reducing the number of imperfect mouldings is of considerable value. The new method of catalysing the hardening of urea resins, described in various modifications in the six patents, is stated to avoid the difficulties found in the admixed-catalyst processes. Further, the resin syrups and the moulding compositions produced by the new method can be stored for long periods, whereas admixed-catalyst materials must be used quite soon after the incorporation of the catalyst.

The new process consists of reacting one molecular proportion of urea with two molecular proportions of formalin by refluxing for about half an hour under neutral or alkaline conditions. Generally ammonia and a trace of caustic soda are part of the reflux liquor. The hardening agents, of which the following list may be taken as typical, are added to the reaction liquor sometimes before and sometimes after condensation:—

- (B.P. 542,932) 1.0 part of monochloroacetyl urea per grammole of urea,
- (B.P. 542,933) 0.1 part of chloroacetonitrile per grammole of urea,
- (B.P. 542,934) 1.0 part of monochloroacetamide per grammole of urea,
- (B.P. 542,972) 1.0 part of monochloroacetone per grammole of urea,
- (B.P. 542,973) 1.0 part of nitro urea with 2.25 parts of sodium nitro urea per grammole of urea,
- (B.P. 542,974) 1.0 part of aminoacetamide hydrochloride per grammole of urea.

The condensation liquor with its added hardening agent is compounded with, for example, 70 parts of alpha cellulose flock and 0.4 part zinc stearate, and dried at 50° C. for 5 hours. The wet composition may be dried in the usual manner either at room temperature or at elevated temperatures in a preheated stream of air or by reflected heat energy. The dried material may be densified by the usual processes of cooking in a Banbury mixer or by rolling or pelleting. The prepared moulding material is moulded at 130° C. at 2,000 lb. per sq. in. in 4 minutes (the thickness of the moulding is not given).

Besides moulding powders the resins can be used in paints, varnishes, enamels, adhesives, anti-crease agents in textiles, laminated materials, and for cast resin products (cf. Chapter X).

There is no discussion in the patents regarding the mechanism of the hardening reaction. All of the hardening agents are stated to be capable of reacting with an aldehyde, and in each patent it is claimed that hardening takes place under non-acid conditions. It is possible that the hardening agents act as cross-linking agents.

Urea-formaldehyde moulding powders are obtainable in translucent and opaque material, in all shades from white to pastel shades and deep colours.

Urea-formaldehyde moulding powders with no filler present are apt to develop surface crazing. When cellulosic fillers are present this crazing is to all intents and purposes eliminated. It is believed that there is some form of chemical combination between the urea-formaldehyde resin and the cellulose, the product being termed glucanure.¹³ Recently, however, unfilled transparent moulding powder has become available and mouldings made from it do not on ageing show to any marked degree the surface-crazing effect.

Urea-formaldehyde resins prepared for moulding powders differ quite distinctly from phenol-formaldehyde resins. At quite an early stage in their preparation phenolic resins become hydrophobe and hence separate out from the aqueous phase; thermo-hardening of this resin consists of changing a thermoplastic hydrophobe resin to a thermo-set hydrophobe resin. On the other hand, urea-

formaldehyde resins are hydrophil and do not separate out from the aqueous phase. In fact they become hydrophobe only when the resin is completely cured. A corollary of this is that water is separated from the urea-formaldehyde resin during the thermo-hardening process.

MOULDING OF UREA-FORMALDEHYDE POWDERS

(From *Beetle, Pollopas, and Scarab Moulding Powders*, British Industrial Plastics.)

Beetle.

Moulds made from ordinary mild steel are suitable for the darker colours, but in order to get a finish free from blemishes with white or translucent mouldings, stainless steel or chromium-plated moulds are recommended. Beetle powders (sulphite wood pulp as filler) are moulded at 240-320° F. (115-60°). The temperature used depends on the nature of the moulding, thickness of its section, and ease of ejection. Simple shapes of thin section, which can be easily ejected, can be moulded at temperatures at the top of the range, since the risk of overcuring is small, and there is the advantage of a shorter curing time. Articles of deep draw, for example a tumbler, require a longer time for flow, so are moulded at lower temperatures. Thick-sectioned mouldings are also moulded at lower temperatures.

An article $\frac{1}{16}$ in. thick should cure in $1\frac{1}{2}$ minutes at 250-60° F.: at 320° F. the rate of cure is twice as fast as at 270° F. At higher temperatures there is a much smaller margin between just cured and overcured, so that curing cycles at higher temperatures must be accurately controlled.

The use of too high a moulding temperature is indicated by:

- (1) Bleaching or whitening on part of the moulded surface.
- (2) Blistering accompanied by bleaching.
- (3) Chalkiness where the moulding has not been properly formed, owing to the powder being pre-cured through excessive heat, and the flowing properties thereby impaired.

Pre-curing is indicated by a whitish bloom at those parts of the moulding where the powder has come into contact with the hot mould and becomes partially cured before pressure has been applied.

For the usual run of mouldings, $1\frac{1}{2}$ tons per sq. in. is generally required, but a moulding with a deep draw requires more pressure. For mouldings in which a portion of the powder has to be forced through a narrow part in the mould, a pressure of 3 tons per sq. in. or more may be required. With pellets the moulding material is localized, receives the pressure direct, and becomes plastic more rapidly than is the case with loose powder.

Mouldings are ejected hot except for large mouldings, flat objects in particular, which should be cooled before ejection.

Beetle powders are very fine, so are not supplied as ready-mixed mottles, since in transit they might become thoroughly mixed and

lose their mottle. Mottled effects are obtained by adding together different coloured powders immediately before moulding.

Pollopas.

Pollopas powder is available in as wide a range of colours as Beetle, but is supplied in powder form only, as it is not suitable for pelleting. Pollopas has low water absorption, so is specially suitable for mouldings which will be in contact with commodities with high liquid content such as certain cosmetic preparations. It is also preferred for lamp-shades.

Pollopas is moulded under the same general conditions as for Beetle, but a little more care is required. Mouldings can be cured at 290–310° F., but at this temperature range it is necessary to breathe the mould. If breathing is not possible, a lower temperature range, 250–60°, must be used. Slow application of the moulding pressure is desirable, and in some cases pre-heating of the powder at 180–212° F. may be advantageous. The moulding time for sections $\frac{1}{8}$ in. thick is from 4 to 5 minutes.

Scarab.

Scarab moulding powder is reputed to be wood-flour filled urea-formaldehyde moulding powder. Scarab is not available in such pale translucent shades as Beetle and Pollopas, but Scarab colours are pale when compared with phenolic moulding powder colours. Scarab blacks and browns are extensively used. Other colours include red, blue, green, yellow, buff, oatmeal, and grey. Scarab powders have the same general properties as Beetle and can be moulded under similar conditions.

Applications for which urea-formaldehyde mouldings are unsuitable are:

- (1) Mouldings which are, under service conditions, subjected to dry heat for prolonged periods, such as, for example, lamp-holders.
- (2) Mouldings coming into contact with battery acid.
- (3) Mouldings with heavy metal inserts.

In addition to the pioneer powders, Beetle, Pollopas, and Scarab, made by Messrs. British Industrial Plastics, Ltd., urea-formaldehyde moulding powders are made by Messrs. I.C.I. (Plastics), Ltd.

Whilst the largest use of phenolic mouldings is for electrical purposes, the largest use for urea-formaldehyde mouldings is for decorative purposes, although electrical insulation parts such as switch covers, lamp-holders, and the like, which have to conform to an interior decorating colour scheme, are very often made in urea-formaldehyde material.

Typical uses of urea-formaldehyde mouldings are for table ware, fruit bowls, tea-trays, lamp-shades, radio cabinets, toilet and cosmetic packing vessels, bottle closures, clock cases, and the like. A recent development has been the production of moulded buttons.

There is no British Standard Specification for the testing of urea-

formaldehyde plastics: according to W. Blakey,¹⁴ the principal tests carried out on urea-formaldehyde moulding powders are:

- (1) Plasticity or flow.
- (2) Speed of cure.
- (3) Apparent density and bulk factor.
- (4) Moisture content.
- (5) Pelleting properties.

In practice, plasticity and speed of cure are intimately connected. Plasticity is measured by the time required to make a given article under specified conditions. The Cup Flow Method (B.S.S. 771, 1938) gives disappointing results with urea-formaldehyde powders, but the flow disc mould method is very useful.¹⁵

The method of injecting a pellet of material into a spiral mould cavity of gradually decreasing cross-section, so that the degree of plasticity can be assessed by the length of the spiral,¹⁶ was widely used in France.

The bulk factor,¹⁴ which is the ratio of the s.g. of the moulding to the apparent density of the moulding powder, is about 4:1 for loose powders and 1.5:1 for densified materials. A powder of low bulk factor has greater apparent plasticity: that is to say, a densified urea-formaldehyde powder flows better than the original powder.

The moisture content¹⁴ of the U.-F. powder is obtained by drying a weighed sample over a dehydrating agent such as concentrated sulphuric acid or phosphorus pentoxide. The water content by this desiccation method is usually about 1 per cent. In addition to this the powders contain about 7 per cent. of water which can be removed by distillation with high-boiling solvents. This water is probably present as methylol groups and hydrophilic water. In moulding, this 7 per cent. of water is liberated during the thermo-hardening reaction and distributed through the moulding. Under dry conditions of service or storing this water is, in part at least, eliminated from the moulding, thus causing a linear shrinkage in dimensions of as much as 0.5 per cent. accompanied by surface crazing.

With regard to the pelleting properties it has been found that powders which pellet well have high plasticity and contain a high proportion of finely ground material.

The degree of cure of a urea-formaldehyde moulding is connected with its water absorption.¹⁴ There is a profound difference between the phenomenon observed with boiling water and that with cold water.

In the boiling-water test¹⁴ the moulding is immersed under standard conditions in boiling water for a standard time between 10 and 15 minutes, and the percentage increase in weight measured. It is found that optimum cure is indicated by a low water absorption and small degree of surface attack. The boiling-water absorption is further decreased with increased moulding time until a stage is reached when the moulding is overcured and burnt.

In the cold-water test¹⁴ the moulding is immersed in cold water for

7 days, and the water absorption value found usually ranges from 0.25 to 0.65 per cent. In this test, however, the water absorption falls to a minimum at a relatively short cure and thereafter rises with further cure.

ELECTRICAL TESTS

The electrical and physical tests on urea-formaldehyde mouldings are in general carried out in accordance with the methods described in B.S.S. 488. An additional electrical test applied to urea plastics is the tracking test, which is designed to show whether an insulator will break down on the surface through the formation of a conducting carbon track. The test is carried out by putting salt solution on the surface of the insulator between two live electrodes. The water boils away, leaving a deposit of salt which may become incandescent. On cleaning off the salt, no sign of tracking is visible. With other types of thermo-setting plastics the tracking starts on the first application of the salt solution.

LAMINATED PRODUCTS¹⁷

For the production of laminated materials a mixed urea/thio-urea-formaldehyde condensate is prepared by reacting in the cold under alkaline conditions and then preferably making slightly acid. It has been found that a straight urea-formaldehyde condensate is not suitable for laminating work, apparently because it heat-cures too quickly. Thio-urea-formaldehyde resins have a slower rate of cure; the presence of a proportion of thio-urea in the condensate used for laminating has been found to slow up the hardening to a workable degree. However, an advantage of having thio-urea present is that the water resistance of the laminates is raised.

High-grade absorbent paper is impregnated with urea/thio-urea-formaldehyde syrup and dried at 190–230° F. to a pre-determined degree. This impregnated paper contains about 50 per cent. resin, and frequently the paper used for the outside layers is given a double impregnation so that its resin content is raised to 60–65 per cent. The high resin content increases the gloss and weather resistance.

The dried impregnated paper is cut to size and assembled in bundles, the thickness of the sheets and the number of the sheets in a bundle determining the thickness of the ultimate laminate.

The bundles are hot-pressed between mirror-polished, satin finish, or patterned stainless steel plates, the surface effect of the steel plate being faithfully reproduced on the laminate. Pressing is carried out at 130–5° in a multiple daylight press, and the material is cooled under pressure before ejecting. The length of time in the press, including heating up, curing, and cooling, is about 2 hours, but the material is maintained at its full curing temperature for about $\frac{1}{2}$ hour only.

In this manner sheets of thickness 0.030 in. to 0.500 in. by 3 ft. by 8 ft. can be obtained. With thin sheets, absolutely uniform pressure must be obtained all over the sheet in order to prevent the formation of underpressed opaque spots. Thin sheets are sufficiently

Physical properties of Mouldings made from Beetle, Beetle Transparent, Scarab, and Pollopas

<i>Test</i>	<i>Beetle</i>	<i>Beetle transparent</i>	<i>Pollopas</i>	<i>Scarab</i>
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 kg. per sq. cm.	560-730	480-560	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 kg. 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 mg. (0.10%)	135 mg. (0.45%)	18 mg. (0.06%)	45 mg. (0.15%)
7 days	150 mg. (0.50%)	..	80 mg. (0.27%)	195 mg. (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 at 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°-95° 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 cub. in.	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	0.008 per linear in.	0.011 per linear in.	0.008 per linear in.	0.008 per linear in.
Coefficient of expansion	0.000045 per ° C. (0.000025 per ° F.)	..	0.000038 per ° C. (0.000020 per ° F.)	0.000043 per ° C. (0.000024 per ° F.)

flexible to be bent round a fairly short radius; when heated they soften somewhat and can be bent to simple shapes such as cylinders, half-cylinders, and 'S' forms.

The laminated sheets obtained in this manner are a translucent pearl colour which turns slightly yellow in sunlight. Opaque and coloured sheets are obtained by incorporating pigments and dyes with the paper before hot-pressing.

Urea-laminated material is used chiefly for constructional work, such as wall-panelling, diffused lighting panels, office partitions, Venetian blind slats, and table tops.¹⁵

REFERENCES

1. B.P. 151,016 (1920).
2. B.P. 208,761 (1922); B., 1924, 63.
3. *Ber.*, 1896, 29, 2438.
4. *Kolloid Beihefte*, 1932, 36, 387.
5. *Kolloid Beihefte*, 1931, 34, 163; *Farben-Chem.*, 1936, 7, 2, 69; *Trans. Faraday Soc.*, 1936, 32, 377, 402.
6. B.P. 535,176.
7. B.P. 171,094, 181,014, 193,420, 201,906, 206,512, 213,567, 217,888, 238,904, 240,840, 248,729, 261,409, 271,037, 291,336, 301,798 (B., 1930, 339), 339,601 (B. 1931, 262)
8. Amer. Cyanamid Co., U.S.P. 2,030,192; B., 1937, 63.
9. I.C.I., B.P. 506,003-4; B., 1939, 861.
10. Bakelite Ltd., B.P. 518,321; B., 1940, 378.
11. *Br. Plastics*, 1941, 12, 141, 283
12. British Thomson Houston Co. Ltd., B.P. 542,932-3-4; 542,972-3-4.
13. C. Ellis, *Chemistry of Synthetic Resins*, 1935.
14. *Chem. Ind.*, 1937, 177.
15. C. Wainwright, *Trans. I.P.I.*, 1937, 6, 12, 13.
16. M. Forer, *Br. Plastics Year Book*, 1933, 68
17. Clark, *Modern Plastics*, 1938, 16, 2, 260; MacHale, *ibid.*, 1938, 16, 2, 266; Stockfish, *ibid.*, 1939, 17, 2, 425.

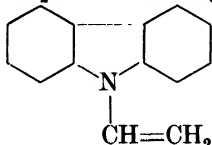
CHAPTER V

VINYL RESINS

By ROWLAND HILL

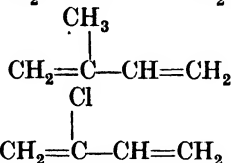
VINYL compounds are defined as compounds which possess the grouping $\text{CH}_2=\text{CH}-$. As illustrating some of the more important vinyl compounds which are used as the basis of synthetic resins, the following may be mentioned:

$\text{CH}_2=\text{CH}\cdot\text{Cl}$	Vinyl chloride.
$\text{CH}_2=\text{CH}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$	Vinyl acetate.
$\text{CH}_2=\text{CH}\cdot\text{C}_6\text{H}_5$	Styrene.
$\text{CH}_2=\text{CH}\cdot\text{O}\cdot\text{C}_2\text{H}_5$	Vinyl ethyl ether.
$\text{CH}_2=\text{CH}\cdot\text{CHO}$	Acrolein.
$\text{CH}_2=\text{CH}\cdot\text{CO}\cdot\text{CH}_3$	Vinyl methyl ketone.



N-Vinyl carbazole.

Acrylic acid $\text{CH}_2=\text{CH}\cdot\text{COOH}$ is likewise to be regarded as a vinyl compound. The importance of the acrylic resins is now such that these merit separate treatment in the following chapter. Butadiene, sometimes called divinyl $\text{CH}_2=\text{CH}\cdot\text{CH}=\text{CH}_2$ and substituted butadienes such as isoprene



and chloroprene

also represent a particular class of vinyl compounds. On polymerization, these dienes result in synthetic rubbers, and are accordingly excluded from further consideration.

This classification if strictly adhered to is not altogether satisfactory since it excludes simple substituted vinyl compounds such as

$\text{CH}_2=\text{C} \begin{array}{l} \diagup \text{Cl} \\ \diagdown \text{Cl} \end{array}$	Asym. dichloroethylene.
$\text{CH}_2=\text{C} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{C}_6\text{H}_5 \end{array}$	α -Methyl styrene.
$\text{CH}_2=\text{C} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CO}\cdot\text{CH}_3 \end{array}$	Isopropenyl methyl ketone.
$\text{CH}_2=\text{C} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{array}$	Isobutylene.

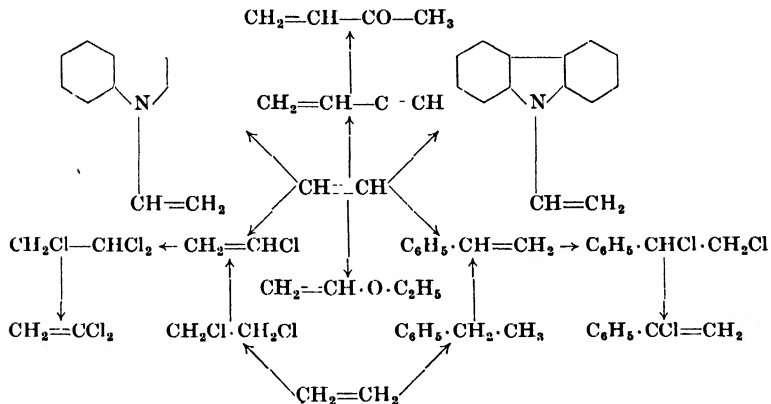
The logic for differentiating on formal grounds is difficult to justify when it is considered that many of these methylene compounds polymerize along similar lines to the vinyl compounds. On this account, the scope of the present chapter is enlarged beyond that set down in the above definition to include such cases.

Vinyl polymers represent one of the most technically important branches in the plastics industry, and it is one which is continually expanding with improvements in technique, in preparation, and with the development of new applications.

The technical and academic literature is most profuse, and it is only possible within the confines of the present chapter to deal with the salient features.

The preparation of vinyl compounds is based primarily upon either acetylene or ethylene, as will be evident from the following diagram.

Preparation of Vinyl Compounds from Acetylene and Ethylene

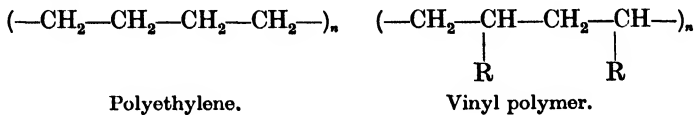


The properties of vinyl polymers depend primarily upon the nature of the substituent group(s), and to a less extent upon the molecular weight. They all possess one feature in common, as they are built up of saturated carbon chains of variable length, containing pendant groupings.

HYDROCARBON POLYMERS

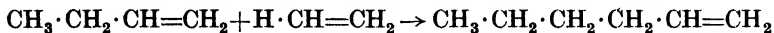
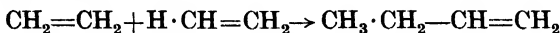
Ethylene.

Polyethylene can be regarded as being the parent of all vinyl polymers,



and is in effect a vinyl polymer in which the substituent grouping R is hydrogen.

Ethylene may be polymerized with certain catalysts; the course of polymerization and the nature of the products are greatly influenced by temperature and pressure of operation. Generally, the products formed are of comparatively low molecular weight (200–400), and vary from mobile to viscous oils according to the precise conditions. Special mention may be made of boron fluoride,² phosphoric acid or its salts,³ organometallic complexes,⁴ silicon and silicon containing substances,⁵ zinc chloride, and aluminium chloride,⁶ all of which under appropriate conditions show a profound catalytic effect. The primary reaction is generally supposed to be stepwise migration,⁷ thus:—



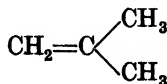
If the conditions are searching in regard to temperature and pressure, secondary reactions occur; thus Ipatiev⁸ working at 400° and 70 atmospheres obtained C₆—C₁₂ saturated and unsaturated hydrocarbons as well as naphthenes (cf. also⁶).

The production of polymers of high molecular weight (2,000–24,000) has recently been accomplished by polymerizing at above 1,200 atmospheres pressure preferably with the aid of a small proportion of oxygen⁹ (cf. Chap. XII, p. 320). Care is necessary to prevent the temperature from reaching a point above which explosive decomposition occurs. In contrast to the liquid and sticky polymers, these polyethylenes are tough and flexible solids. Films and tapes can be made by hot-pressing or moulding the polymer above 110°, at which point polyethylene softens sharply,¹⁰ and mouldings by the usual injection moulding technique.¹¹ Threads can be produced by extruding the molten polymeride, and these are greatly improved mechanically by cold drawing.¹² By employing this high-pressure technique, ethylene has been interpolymerized with many other unsaturated compounds, to give a wide range of interpolymers, the properties of which are determined by the nature and amount of the compound employed.¹³

Some of these are low softening solids, whereas others, e.g. those from styrene and glycol methacrylate, are hard. Chlorination of polyethylene gives rise to products which vary from rubbery to horn-like materials according to the degree of chlorination.¹⁴

Polyethylene is yet in its infancy, and many novel applications are likely to be developed. In particular its excellent electrical properties make it valuable as a sheathing for high tension cables, and as a spacer for co-axial cables of zero impedance (V/I).¹⁵

Isobutylene.



Isobutylene is readily prepared by dehydration of tertiary butyl alcohol, using comparatively mild dehydrants such as anhydrous oxalic acid. It is also obtained by dehydration of isobutyl alcohol, though in this case the reaction does not proceed with such readiness, and the product is accompanied by the isomeric butylenes. Isobutylene occurs to a certain extent in the refinery gases in the cracking of petroleum hydrocarbons. It may be produced from the normal butylenes which are more abundant, under the influence of isomerizing agents, for example phosphoric acids¹⁶ at elevated temperatures. Isobutane also provides a source of isobutylene; dehydrogenation proceeds smoothly at high temperatures with the aid of catalysts such as promoted chromium oxide catalysts.¹⁷

A wide range of polymers has been produced from isobutylene, which range from oils with desirable fuel characteristics to highly rubber-like products, according to the conditions of polymerization. Thus, hot moderately concentrated sulphuric acid results in high yields of the open-chain dimer di-isobutylene (2-2-4-trimethylpentene),¹⁸ which on hydrogenation affords a very valuable motor fuel having a high anti-knock rating. Polymers which are rather more complex, but which nevertheless are still liquid, are produced by polymerization at high temperatures and pressures, e.g. 180–250° at 100 atmospheres;¹⁹ these are also used as motor fuels. The most important catalysts are boron trifluoride and aluminium chloride. At ordinary temperatures these agents bring about rapid polymerization, leading to low molecular weight polymers which are viscous oils, or sticky solids. However, by reducing the temperature of polymerization, there is a marked increase in molecular weight, and when the operation is conducted at –80° to –100°, as by using carbon dioxide snow or liquid ethylene as the refrigerants, polymers of high molecular weight are formed.²⁰ Although boron fluoride appears to be the preferred catalyst, aluminium chloride, particularly in the form of complexes such as with ethyl chloride, has been mentioned.^{21, 22} The rate of polymerization and the yield are improved by using small amounts of secondary agents such as acids, phenols, and amines.²³ High molecular weight polyisobutylene is produced commercially under the names Oppanol and Vistanex. It is a colourless thermoplastic elastic product which resembles natural rubber in many respects though it cannot be vulcanized; the electrical properties are excellent. Mixtures of rubber and polyisobutylene when vulcanized have a high corona and ozone resistance.²⁴ Various applications have been proposed, as for example in submarine cables,²⁵ as a sandwich in safety glass,²⁶ as a thickening agent for lubricating oils,²⁷ and for moulding compositions when admixed with polyvinyl chloride and acetate polymers and interpolymers,²⁸ and with indene and coumarone resins.²⁹ Polyisobutylene may be chlorinated readily, the properties of the chlorinated polymers resting upon the degree of chlorination; thus, polymers containing a high proportion of chlorine are resinous and dissolve in drying oils.^{30, 31}

Styrene. $C_6H_5 \cdot CH=CH_2$.

Preparation. Styrene was first prepared in 1831.³² The method commonly employed by early academic workers was to heat cinnamic acid ($C_6H_5 \cdot CH=CH \cdot COOH$) under conditions whereby carbon dioxide is eliminated. Barium hydroxide,³³ copper,³⁴ hydrogen bromide and alkali,³⁵ and even careful distillation³⁶ bring about or assist in the transformation. Another method mainly of academic interest consists in dehydrating β -phenylethyl alcohol; ($C_6H_5 \cdot CH_2 \cdot CH_2OH$), anhydrous potassium hydroxide affords styrene almost quantitatively.³⁷ The isomeric α -phenylethyl alcohol ($C_6H_5 \cdot CHOH \cdot CH_3$) does not dehydrate with such readiness. Phosphoric acid is a suitable dehydrant.³⁸ Vapour-phase dehydration over the usual dehydrating catalysts such as alumina, gives particularly good yields of styrene.³⁹

The most important technical methods are based upon ethyl benzene, which is readily produced by condensation of ethyl chloride with benzene in the presence of aluminium chloride, or by direct condensation of ethylene with benzene using the same agent.⁴⁰ The ethyl benzene may then be dehydrogenated directly to styrene, or chlorinated to monochloroethyl benzenes followed by dehydrochlorination. The former method, although more direct, suffers from the disadvantage that the boiling-points of styrene and ethyl benzene lie close to one another, so that separation becomes very difficult. One method which has been proposed for effecting the separation is to cool the mixture to -30° to -60° , when crystals of pure styrene separate.⁴¹ The direct conversion of ethyl benzene into styrene is brought about by passage through a hot tube at 650° ; conversion does not exceed 30 per cent.⁴² In order to increase the conversion and to minimize undesirable side reactions, various dehydrogenating catalysts have been proposed such as silica gel and active carbon;⁴³ cerium, copper, iron, and zinc oxides,⁴⁴ which may be promoted by tungsten, molybdenum, or uranium oxides.⁴⁵

When ethyl benzene is chlorinated at low temperatures it gives essentially a mixture of α - and β -chloroethyl benzenes⁴⁶ which are readily separable from any unchanged ethyl benzene. Removal of hydrogen chloride from the chloroethyl benzenes may then be effected in a variety of ways: by passing over active carbon at 260° ;⁴⁷ by heating with organic bases,⁴⁸ mercury salts or zinc chloride,⁴⁹ weak organic acids,⁵⁰ or strong acids such as sulphuric and phosphoric acids.⁵¹ A recent process of outstanding interest consists in passing acetylene and benzene through a reaction zone at 800 – $1,000^\circ$ under sub-atmospheric pressure, whereby styrene is formed directly.⁵²

The maximum yield of ethyl benzene is 50 per cent. (calculated on the ethylene), while a considerable amount of polyethyl benzene is formed. The yield is raised to 61.5 per cent. and the polyethyl benzenes to 8 per cent. by operating in the presence of about 40 per cent. of propylene.

Polymerization. The polymerization and interpolymerization of

styrene with other unsaturated compounds has probably been studied more intensively than any other vinyl compound. The first observations were made as early as 1839-45 by Simon⁵³ and Hofmann.⁵⁴ The latter noted that styrene passed into a glassy solid on heating, and under the influence of light. Some time later,⁵⁵ it was shown that the same change occurred in the dark at ordinary temperatures, but much more slowly. One of the earliest serious attempts to arrive at an understanding of polymerization processes appears to have been based upon styrene, firstly on the part of Kronstein⁵⁶ and later by Stobbe.^{57, 58} Viscosity and refractive index were used as a means of following the changes. Prior to the classical researches of Staudinger dating from 1926, knowledge on styrene polymerization was very limited. Since that date an abundant literature on the subject has made its appearance. A wide variety of methods have now been described for effecting and controlling the operation, and for influencing the properties of the polymers.

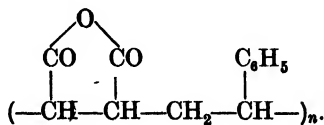
The important factors for affecting the rate of polymerization and the molecular weight of the polymer are temperature, nature and amount of catalyst, light, presence or otherwise of diluents, and pressure. In a general way, the more rapid polymerization proceeds the lower is the molecular weight of the resulting polymer. Styrene is unique amongst vinyl compounds in the breadth of polymers it affords. Thus by appropriate choice of polymerization conditions Staudinger has shown that products from dimer through polymers of varying mean molecular weights to an upper limit of around 600,000 can be realized.⁵⁹

Pure styrene polymerizes extremely slowly at ordinary temperatures, and even after several years is incompletely polymerized. In order to obtain a practicable rate of polymerization in the absence of catalysts, it is necessary to heat to around 100° or higher.⁶⁰ Polymerization is a reversible process; when styrene polymer is heated to temperatures above 300° it is depolymerized to monomer.⁶⁴ Hence styrene cannot be polymerized at such high temperatures.

Catalysts fall into fairly well-defined classes. The most important class is the oxygen donating class such as oxygen, organic peroxides, e.g. benzoyl peroxide,⁶¹ perbenzoic acid,⁶² benzoyl hydrogen peroxide,⁶³ hydrogen peroxide,⁶⁴ ozonides,⁶⁵ and ozone.⁶⁶ The use of these catalysts enables polymerization to be carried out at considerably lower temperatures, and to complete the operations rapidly. The oxygen-donating catalysts are generally preferred since they do not impair the colour or the homogeneity of the polymer. Inorganic halides such as aluminium chloride,^{67, 68} stannic chloride, boron trifluoride, and phosphorus oxychloride,^{69, 70} and hydrogen fluoride⁷¹ are all particularly active. Thus, 3 per cent. stannic chloride causes very vigorous polymerization at 0°, and it is difficult to prevent the temperature from rising unduly. Amongst the miscellaneous catalysts special mention may be made of active earths, e.g. Florida earth,⁶⁹ alkali metals,⁷² carbonyls of the heavy metals,⁷³ lead tetraethyl,⁷⁴ and aryl diazonium fluoborates.⁷⁵ The amount of catalyst

employed depends upon the nature of the catalyst and the temperature of polymerization. Generally it is not necessary to employ more than 2 per cent., and in most cases considerably less than this will suffice. Styrene is subject to the influence of light; ordinary light accelerates polymerization, whilst ultra-violet light is very effective.⁷⁶ The addition of photo-sensitizers still further accelerates photochemical polymerization. Benzophenone is, it is claimed, a particularly active photosensitizer; a comparatively small addition is required, and polymerization is complete in a few hours at 60–70°.⁷⁷ Polymerization can be carried out in a solvent for the monomer and polymer, e.g. toluene or ethyl benzene, the latter solvent being particularly convenient, since it is then no longer necessary to separate styrene from ethyl benzene.^{78, 79} Polymers formed in the presence of solvents are of lower molecular weight than those produced by mass methods, and generally are not so tough. It has been shown that the nature and amount of solvent employed has quite a profound effect.⁸⁰ High pressures favour the polymerization of styrene, but the effect is not sufficiently marked to be of technical importance.^{81, 82} Polymerization may also be effected in aqueous emulsion whereby the polymer is produced in latex form (cf. Chap. XIII, p. 371).⁸³ It is then possible to remove volatile impurities such as ethyl benzene and unpolymerized styrene by steam-blowing the latex.⁸⁴ A defect of polystyrene is a tendency for mouldings and castings to develop fine cracks—known as ‘crazing’. It is said that this is due to the evaporation of low molecular weight polymerides, and may be obviated by polymerizing at temperatures gradually rising from 40° to 160° during 15–20 days, followed by heating in vacuum at 170–5° for 5 hours.⁸⁵

The properties of styrene polymer can be modified and within limits controlled at will by interpolymerization. Interpolymerization is effected by mixing styrene with a second unsaturated substance, not necessarily polymerizable by itself, and heating the mixture usually in the presence of a catalyst, either with or without a solvent, or in aqueous emulsion. The properties of the interpolymers are frequently unexpected and quite different from mixtures of the parent polymers. By appropriate selection of the nature and amount of the unsaturated substance, interpolymers with a wide range of properties have been devised. Wagner-Jauregg⁸⁶ was the first to make use of this technique. On heating together styrene and maleic anhydride a homogeneous mass was obtained which differed from styrene polymer in being insoluble in benzene, but soluble in alcohol and aqueous alkali (cf. also⁸⁷). The constitution of this interpolymer was represented as consisting of a long chain made up of alternate styrene and maleic anhydride units:



Staudinger⁸⁸ has shown that small amounts even as low as 0.02 per cent. of divinyl benzene co-polymerized with styrene lead to products which are no longer soluble in solvents, but which swell more or less strongly according to the proportion of divinyl benzene present. This effect is attributed to the occasional cross linking of chains as a direct consequence of the bifunctional nature of divinyl benzene, as shown in the scheme on p. 434.

On account of this, it is essential that styrene monomer should be rigidly purified from divinyl benzene in technical practice, which may be formed from diethyl benzene, produced in the ethylation of benzene. The properties of styrene polymer can be improved by introducing relatively small amounts of selected unsaturated substances. For example, up to 5 per cent. acrylo- or methacrylonitrile improves heat resistance and mechanical properties.⁸⁹ In certain systems, particularly where styrene is present in minor amount, the properties of styrene polymer are entirely overshadowed, as in the interpolymers with butadiene.⁹⁰ In this case, the interpolymers are synthetic rubbers. It is beyond the scope of this chapter to enumerate the various interpolymers of styrene which are known, but particular mention may be made of the products derived from vinyl chloride,⁹¹ vinyl ethers and esters,⁹² acrylic esters,⁹³ and unsaturated ketones.⁹⁴ The polymerization of styrene may be conducted in the presence of miscellaneous agents such as dyestuffs,⁹⁵ colloidal metals,⁹⁶ fillers,⁹⁷ thereby providing a convenient method of bringing these into intimate solution or dispersion with the polymer. Finally, styrene has been polymerized in the presence of rubber latex⁹⁸ and drying oils,⁹⁹ to produce products in which possibly some combination has occurred.

Properties and Applications. The properties of polystyrene are determined by the molecular weight. The low molecular weight polymers (e.g. 3,000) are comparatively brittle, and dissolve in some of the solvents in which the higher molecular weight polymers are insoluble. These polymers soften fairly sharply, forming mobile liquids. As the molecular weight is increased, the products become progressively tougher and harder and diminish in solubility. The softening point tends to increase, and the products then exhibit plastic rather than liquid flow. The high molecular weight polymers are rubber-like when softened,⁵⁹ and when precipitated from solution separate in fibrous form.

Technical polystyrene is colourless, light-fast, transparent, hard (Mohr, 2-3), tough, and thermoplastic (softens at 80°). It has a low specific gravity (1.06) and a high refractive index. The outstanding feature of polystyrene is its excellent electrical properties. It is soluble in aromatic hydrocarbons, chlorinated hydrocarbons and esters, but insoluble in aliphatic hydrocarbons and alcohols. Resistance to strong acids and alkalis is exceptional, and permeability to moisture is low. High molecular weight polystyrene is normally incompatible with drying oils and varnish diluents, but recent work upon the control of the polymerization has shown that under appro-

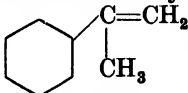
priate conditions, oil-soluble polymers can be produced.¹⁰⁰ These oil-soluble styrene polymers can be combined with drying oils to give oil varnishes combining excellent flexibility and film strength with high resistance to moisture absorption and moisture permeability. They also retain good colour, show high stability to heat, acids, and alkalis, and have a high dielectric breakdown. Polystyrene is unsuitable for general use as a coating composition on account of poor durability. This can be improved by the addition of plasticizers,¹⁰¹ such as tricresyl phosphate, dibutyl phthalate, glycerol dibenzyl ether, butyl stearate,¹⁰² and phthalide and its derivatives,¹⁰³ and by the addition of certain other resins such as coumarone, ester gum, and dammar.¹⁰⁴ Various applications have been proposed for suitably compounded polystyrene lacquers based upon the good waterproofing and electrical properties; for example, waterproofing articles made from cellulose esters,¹⁰⁵ and shot-gun shells,¹⁰⁶ for impregnating electrical equipment,¹⁰⁷ and as an insulating medium for submarine cables.¹⁰⁸ It has been proposed as a delustring agent for rayon, and for stiffening the handle of textile fabrics and making them less susceptible to water spotting.¹⁰⁹ Polystyrene is not compatible with cellulose esters or ethers.

The main outlet at present lies in the production of mouldings having especially good electrical properties, as for example, in the construction of panelling and coils for short-wave radio apparatus. Polystyrene is particularly suited to injection moulding¹¹⁰ on account of the freedom with which it flows under moulding conditions. A temperature of 140–80° is recommended under a pressure of 1,000 lb. per sq. in. Mouldings have a high shock-resistance. The thermal expansion and contraction is small, which is of particular advantage in the production of mouldings. One disadvantage of polystyrene, previously referred to, is the development of very fine superficial cracks in the mouldings after an interval of time, known as 'crazing'. It has been claimed that this is avoided by admixture with diphenyl chloride.¹¹¹ By subjecting polystyrene to drawing as it is being extruded in the form of a thin foil, the mechanical forces cause adlineation of the molecules, and the physical properties of the drawn polymer are then quite different. Thin films and foils are flexible, and exhibit a certain degree of elongation.¹¹² In this form, the material is in a particularly useful condition for use as a cable-insulating medium.

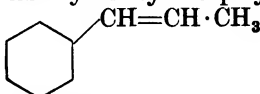
Polystyrene can be subjected to various chemical reactions. Staudinger has hydrogenated the polymer at high temperatures in solution in the presence of nickel catalyst, but some cracking occurred;¹¹³ by working under more moderate conditions this was avoided.¹¹⁴ The hydrogenated polymer is more resistant to heat,¹¹⁵ and is of value as an addition to lubricating oils. On sulphonation with chlorosulphonic acid, sulphonated polymers are produced which are claimed to be useful as wetting, emulsifying, and sizing agents.¹¹⁶ Chlorination reduces thermoplasticity.¹¹⁷

Miscellaneous Hydrocarbon Polymers.

When the α -hydrogen atom in the styrene side chain is substituted by a methyl group, the tendency to polymerize is markedly reduced.

Thus α -methyl styrene (isopropenylbenzene)  does not

polymerize on long standing or by the action of light. In order to bring about polymerization stannic chloride is employed as catalyst, and the molecular weight of the so formed polymers is low.¹¹⁸ In fact the low molecular weight polymers of α -methylstyrene have been proposed for improving the flexibility of styrene polymers.¹¹⁹

β -Methyl styrene (propenylbenzene)  is even

more stable and does not respond to the action of stannic chloride. Under the influence of boron fluoride, a transparent but brittle polymer of low molecular weight is formed.¹²⁰

Little information is available concerning the *vinyl naphthalenes*. Palfray has noted that α -vinyl naphthalene polymerizes more readily than styrene.¹²¹

VINYL ESTERS

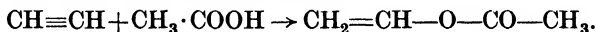
Historical.

Vinyl esters are formed by esterification of the hypothetical vinyl alcohol $\text{CH}_2=\text{CHOH}$ with an acid. Vinyl alcohol has never been isolated as such, since it passes immediately into acetaldehyde. Removal of the elements of water from acetaldehyde or the hypothetical vinyl alcohol gives acetylene. In this sense, acetylene can be used under appropriate conditions as the source of the vinyl radical.

The history of the vinyl resins dates to 1835,¹²² when Regnault first prepared vinyl chloride as a low boiling liquid b.p. -11° , by treating ethylene dichloride with alcoholic potash. He noted the formation of a white powder when sealed tubes of the monomer were exposed to sunlight. In 1872, Baumann¹²³ observed the formation of a tough amorphous insoluble polymer under the influence of light. It was not until 1912 that Ostromislenski pointed out that polyvinyl halides existed in several modifications,¹²⁴ and applied for the first patent in this field for polymerizing vinyl chloride and bromide. The same author shortly after described experiments on the polymerization of vinyl chloride and bromide by irradiation using a mercury vapour lamp. The polymers were described as dispersing in naphthalene, camphor, and hexachloroethane, affording products closely resembling ebonite, celluloid, and gutta-percha.¹²⁵ Ostromislenski appears to have been the first to appreciate the potentialities of the polyvinyl halides. In 1922 Plotnikov showed that certain metallic salts, particularly uranium salts, assisted in the photopoly-

merization of vinyl chloride;¹²⁶ he considered the polymer to be $(\text{CH}_2=\text{CHCl})_{16}$. The polyvinyl halides have been slow to develop technically, probably because of their high softening point, tendency to discolour and decompose unless prepared under well-regulated conditions, and because of their low solubility in organic solvents. In 1928 Flumiani¹²⁷ made an observation which was to prove of considerable significance; he found that polyvinyl chloride made by photopolymerization dispersed slowly in certain hot liquids such as Peru balsam, rosemary oil, and tetralin, which on cooling formed elastic gels. Since this time well over a hundred patents have been issued in Great Britain covering various methods for making vinyl chloride, polymerizing, and utilizing the polymer. It is marketed in various forms under the names, Koroseal, Flamenol, Vinylite, Igelite, Mipolam, and Welvic.

Vinyl acetate was prepared for the first time in 1912 by Chem. Fabrik Griess-Elektron.¹²⁸ by passing acetylene into glacial acetic acid containing mercuric sulphate as catalyst. It was isolated as a liquid b.p. 73°. The same firm shortly afterwards patented the use of oxygen or peroxides for polymerizing vinyl acetate,¹²⁹ this being apparently the first reference to the use of the now highly important class of peroxides as catalysts for vinyl compounds in general. Polymerized vinyl acetate was the first of the vinyl polymers to be manufactured technically. It was introduced in Germany in 1915, but failed to find favour and was discontinued for a period of years.¹³⁰ The development of polyvinyl acetate in America was to some extent accidental. A study of the reaction between acetylene and acetic acid was initiated in 1917 at Shawinigan with the object of producing ethylidene diacetate, a solvent and potential source of acetic anhydride.¹³¹ Vinyl acetate was produced as a by-product in the presence of mercury salts as catalysts.

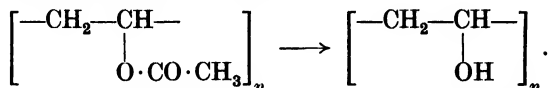


This eventually became of interest for making resins, and methods were developed which gave the unsaturated ester as the principal product. Polyvinyl acetate is now manufactured under various names—Mowilith, Gelva, Vinnapas, and Vinylite.

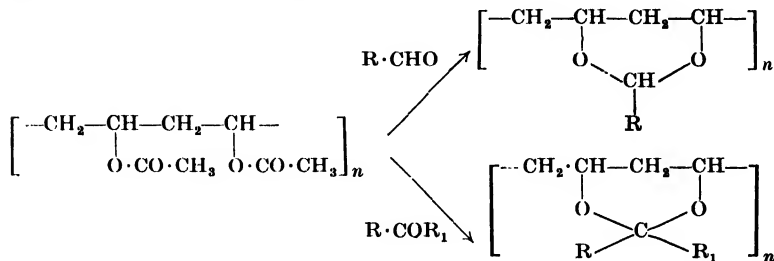
In the broad field of synthetic polymers, the principle of interpolymerization has come to be recognized as one of the most important methods for producing polymers with special effects. Well over a hundred patents have been issued in Britain during the past ten years, covering various desirable combinations. The possibilities of interpolymerization appear to have been recognized first, about 1927, and related to vinyl chloride and vinyl acetate.¹³² Selected interpolymers were shown to have a superior combination of properties compared with the individual polymers. These interpolymers are now manufactured under the name Vinylite.

Although, as already mentioned, vinyl alcohol does not exist as

such, polyvinyl alcohol can be prepared by hydrolysis of polyvinyl acetate, using either acids or alkalis.



A further reaction of considerable importance lies in the interaction between polyvinyl acetate and aldehydes and ketones which give rise to the polyacetals and polyketals.



These are known commercially as Alvar, Vinarol, and Butacite.

Vinyl Chloride.

Preparation. Two methods are available for the preparation of vinyl chloride; direct interaction of acetylene and hydrogen chloride, and removal of hydrogen chloride from ethylene dichloride.

The former method usually involves interaction in the vapour phase, in the presence of suitable catalysts. The most favoured catalysts are mercury salts supported on various substrates¹³³⁻⁵ and active carbon.^{136, 137} Yields of over 90 per cent. are obtained under appropriate conditions.¹³⁸ The reaction may also be conducted in the liquid phase. For example, calcium carbide is heated with concentrated hydrochloric acid in the presence of a mercury catalyst,¹³⁹ and acetylene is passed through a dilute solution of hydrochloric acid containing cuprous and calcium chlorides.¹⁴⁰

The splitting of hydrogen chloride from ethylene dichloride can likewise be conducted by liquid or vapour phase methods. According to the former, ethylene dichloride is heated with a strong alkali such as aqueous caustic soda,¹⁴¹ aqueous alcoholic caustic soda,¹⁴² or methanolic caustic soda.¹⁴³ The vapour-phase process consists simply in passing ethylene dichloride through a heated tube packed with pumice.¹⁴⁴ The temperature of splitting is reduced by employing catalysts, for example, alumina¹⁴⁵ and active carbon.¹⁴⁶

Polymerization and properties of polymers. Vinyl chloride can be polymerized under a wide variety of conditions. The most important methods are as follows:

1. Mass or homogeneous polymerization, in which the monomer is heated with a catalyst, or is exposed to the influence of actinic radiation.

2. Solution polymerization, in which a solvent is introduced, which may be a solvent or a non-solvent for the polymer.
3. Emulsion polymerization, whereby the vinyl chloride is formed into an aqueous emulsion with suitable emulsifying agents, and polymerized in this condition.

The properties of polyvinyl chloride are dependent in the main upon the molecular weight of the polymer, which is determined by the mode of polymerization, temperature, nature and amount of catalyst, and other subsidiary factors. The low molecular weight polymers are soluble in a wide range of solvents, but are relatively brittle, and tend to discolour readily under the influence of heat and light. On the other hand, the high molecular polymers are scarcely soluble in organic solvents; they soften at a high temperature and tend to be rather intractable. Ostromislenski¹⁴⁷ was the first to recognize that such differences existed. Progressive polymerization by the mass method under the action of ultra-violet light was shown to lead to four modifications, differentiated as follows: wide range of solubility (α -polymer); restricted solubility (β -polymer); insoluble but swells (γ -polymer); insoluble not swollen (δ -polymer). Polymerization is usually heterogeneous, the polymer separating as a white powder. Staudinger¹⁴⁸ later investigated this method of polymerization, and separated polymer mixtures by fractional precipitation, showing that the differences in solubility were in step with molecular weight. More uniform products are obtained by interrupting polymerization before completion.¹⁴⁹

When polymerization is carried out in an organic solvent, the polymer may remain dissolved or separate as a white powder, depending upon the nature of the solvent, and the molecular weight of the polymer. Thus, high temperature polymerization in benzenoid hydrocarbons, using benzoyl peroxide catalyst, proceeds to a low molecular weight polymer which remains dissolved in the solvent.¹⁵⁰ By polymerizing in alcohols or ketones at a temperature below 60°, the polymer is progressively precipitated from solution.¹⁵¹ The nature of the solvent has a marked effect, solvents with high dipole moments favouring the formation of longer chain molecules.¹⁵²

Emulsion polymerization is conducted using emulsifying agents such as sodium α -hydroxy-octadecane sulphonate, preferably at pH 3 at 40–5°.¹⁵³ The polymer is produced in a latex-like dispersion from which the polymer can be isolated by addition of brine, which causes coagulation of the latex (cf. Chap. XIII, p. 371). Vinyl chloride may also be polymerized by passing the gas in a finely distributed form through a tower containing a suitable catalyst, notably potassium persulphate.^{154, 155}

When high molecular weight polyvinyl chloride is heated to a temperature of 130° or higher with plasticizers, the polymer is dispersed, and the homogeneous mass sets on cooling to a tough resilient rubber-like gel.¹⁵⁶ This unique behaviour has led to the technical development of plasticized polyvinyl chloride as a rubber-like plastic.¹⁵⁷ In preparing these compositions, the polymer in a finely divided con-

dition is worked with the plasticizer under mechanical pressure such as in an internal mixer or two-bowl mill while the temperature is raised to about 130°. ¹⁵⁸ Alternatively, the polymer is cold-mixed with the plasticizer, and the heterogeneous paste then applied as a coating to any desired surface, and gelatinized by heating. ¹⁵⁹ The properties of plasticized polyvinyl chloride are to some extent determined by the nature as well as the amount of the plasticizer. Tricresyl phosphate and dibutyl phthalate are frequently employed, ^{156, 157} but a variety of less accessible plasticizers have been described for special purposes. Thus alkyl or cyclo-alkyl-tetrahydronaphthalenes are used for especially good electrical properties; ¹⁶⁰ esters of a straight chain aliphatic alcohol and an aromatic carboxylic acid, e.g. dodecyl benzoate, confer freedom from brittleness at low temperatures; ¹⁶¹ ricinoleic acid and acetylated ricinoleic acid improve heat resistance. ¹⁶²

The heat stability of polyvinyl chloride is adversely affected by the presence of low molecular polymers, and solvent extraction with selective solvents has been proposed as a means of improvement. ¹⁶³ By interpolymerizing a small amount of acrylic or methacrylic acids (0.5–3.0 per cent.) with vinyl chloride, and subsequently after treating the interpolymer with dilute alkali, products with superior heat resistance are produced. ¹⁶⁴ Many types of compounds have been described which function as heat stabilizers for polyvinyl chloride, including ethylene oxide compounds, e.g. phenyl glycide ether; ¹⁶⁵ basic organic substances, e.g. diphenylguanidine, ¹⁶⁶ and substances which form hybrid ions, e.g. glycine; ¹⁶⁷ metal soaps, e.g. lead stearate; ¹⁶⁸ and lead or tin aryl or alkyl compounds, e.g. lead tetrapropyl. ¹⁶⁹

Polyvinyl chloride is a snow-white powder, insoluble in most organic solvents. Chlorinated aliphatic hydrocarbons dissolve the polymer when heated, but the solutions tend to form a gel on cooling unless the solutions be very dilute. Dioxan and tetrahydrofuran are the best solvents. The chemical resistance towards acids, alkalis, and oxidizing agents is remarkable. The chlorine atoms are much more difficult to replace by other groups than in lower molecular compounds. Potassium permanganate, chromic acid, and even nitric acid have comparatively little action. ¹⁷⁰ The polymer is thermo-plastic and may be moulded under pressure at temperatures of 150–170°. The mouldings are transparent and coloured yellowish-brown. The unplasticized polymer has a density of 1.3; Martens index, 70; breaking stress (kg. per sq. cm.), 600; Brinell hardness (kg. per sq. cm.), 1,000. The electrical properties are very good.

Electrical properties of polyvinyl chloride

<i>Temperature</i>	<i>Dielectric loss</i>	<i>Dielectric constant</i>	<i>Specific resistance</i>
20	0.02	3.5	10 ¹⁵ per cm.
40	0.02	3.5	10 ¹⁵ „
70	0.023	4.0	10 ¹⁵ „

Breakdown voltage is of the order 28–32 kV per mm. ¹⁷¹

The properties of plasticized polyvinyl chloride depend naturally upon the nature and amount of plasticizer employed. It is customary to employ 35–50 per cent. plasticizer, which is selected according to the particular requirements of the resulting plastic. Such compositions are essentially rubber-like in properties. An outstanding feature is their resistance to ageing; for instance, unlike most rubber-like materials, they are not affected by ozone.

Applications. Although polyvinyl chloride has only been introduced comparatively recently, it is already finding many interesting technical applications.

The pressure-moulded unplasticized polymer has been proposed for pipes, tubings, and jointings of chemical plant which have to withstand the action of strong acids or alkalis. Various methods of producing polyvinyl chloride threads have been described. Thus solutions of polyvinyl chloride are subjected to wet spinning by passing through a precipitating bath whilst stretching the strongly swollen thread.¹⁷² The importance of orienting the polymer during the spinning has been emphasized.¹⁷³ Twists are produced by leading the fibres over hot surfaces and twisting them in the plastic condition.¹⁷⁴ These fibres are of good appearance, fineness, and strength, and are initially non-inflammable; their comparatively low softening point is a disadvantage for many purposes.^{175, 176}

Plasticized polyvinyl chloride is particularly attractive as an insulating material for cables¹⁷⁷ on account of its resistance to chemical influences, oils and solvents, ozone, electrical properties, and non-inflammable nature.¹⁷⁸ Unlike rubber, fillers do not have any reinforcing action; the mechanical strength diminishes with the percentage of fillers incorporated, and the nature of the latter. On this account, the compositions are only lightly filled. Very bright colours can be obtained by appropriate use of colouring matters. The compositions are extruded over cables on standard roving machines, and is more rapid than with rubber.¹⁷¹ Only a slight thickness of the insulating material is necessary, which permits reduction in weight in the finished cable.

Textiles can be prepared with polyvinyl chloride plasticized with chlorinated hydrocarbons such as chlorinated diphenyl,¹⁷⁹ and multiple fabrics are produced with an interlayer of polyvinyl chloride.¹⁸⁰ Miscellaneous applications include porous heat and sound-insulating systems;¹⁸¹ in photographic films;¹⁸² safety glass;¹⁸³ and artificial leather.¹⁸⁴

When polyvinyl chloride is chlorinated in suspension or solution in carbon tetrachloride or tetrachloroethane, the chlorinated polymer becomes soluble in cheap lacquer solvents.¹⁸⁵ The product may be separated in the form of a dense white powder from the solution in which chlorination has been conducted by strongly cooling the solution and adding a non-solvent, or by extruding the solution gelled by chilling into a non-solvent.¹⁸⁶ The improvement in solubility is attributed in part to degradation of the chains.¹⁷⁰ Chlorinated polyvinyl chloride has been proposed as a basis for non-inflammable

photographic films,¹⁸⁷ as a medium for paints, lacquers, and varnishes,¹⁸⁸ adhesives,¹⁸⁹ and fibres and threads.¹⁹⁰

Vinyl chloride interpolymers. Many vinyl chloride interpolymers have been described, the properties of which vary widely according to the nature and amount of the interpolymer component. Generally, interpolymerization follows closely the procedures already described for vinyl chloride alone. The most important interpolymers are those produced with vinyl acetate and methyl acrylate.

The vinyl chloride:vinyl acetate interpolymers fall broadly into two classes—those containing a major proportion of vinyl chloride which are valuable as thermoplastic moulding compositions¹⁹¹ and for the production of artificial threads and fibres;¹⁹² and those containing a minor amount of vinyl chloride which are more suitable as coating compositions.¹³² The influence of the minor amount of vinyl acetate is to lower the softening point of the straight polymer into a region which makes the product generally suitable as a moulding composition; it improves the heat stability and solubility in solvents, but detracts somewhat from water resistance and electrical properties. These interpolymers are colourless, transparent, odourless, tasteless, and non-inflammable. They can be calendered and extruded as rods or tubes, and moulded by standard methods. On account of low shrinkage, large objects such as doors and wall panels can be moulded successfully.¹⁹³ These interpolymers have been used extensively in the production of sound records and dentures.¹⁹⁴ The constants including moulding conditions, hardness, water absorption, and electrical properties have been summarized as follows:¹⁹³

	Filled	Unfilled
Moulding pressures (lb. per sq. in.)	250-2,000	1,200-1,800
Moulding temperatures (° C.)	120-50°	115-30°
Impact (Izod), notched (ft. lb.)	0.10-0.70	0.10-0.45
Impact (Izod), unnotched (ft. lb.)	0.80-1.50	2.0-4.0
Tensile strength (lb. per sq. in.)	6,000-7,500	8,000-10,000
Modulus of elasticity × 10 ³ (lb. per sq. in.)	5.5-8.5	3.5-4.0
Modulus of rupture × 10 ³ (lb. per sq. in.)	7.5-11.0	10.0-13.0
Brinell hardness number (550 lb.—3 min.)	15.0-25.0	10.0-15.0
Specific gravity	1.3-2.5	1.35
Softening-point (° C.)	60-70	50-65
Water absorption at room temperature, per cent. increase in weight:		
24 hrs.	0.20-0.70	0.05-0.15
48 hrs.	0.30-1.10	0.10-0.20
168 hrs.	0.70-1.80	0.15-0.25
Refractive index	1.52-1.53
Volume resistivity (ohms cu. cm.)	10 ¹¹	> 10 ¹⁴
Dielectric constant (volts per mil), 25° C.	350-400	400-500
" " (instantaneous step)	300-50	325-45
Dielectric constant (1,000,000 cycles)	4	4
Power factor (1,000,000 cycles)	6.2%	1.75%
" " (1,000 cycles)	2.15%	1.43%

For the production of textile fibres the interpolymer should have an average molecular weight of at least 15,000,¹⁹² and should prefer-

ably contain 88–90 per cent. vinyl chloride.⁷⁴ The resin is dissolved in a suitable solvent such as acetone, then spun, using standard practice as for acetate silk. It is essential that the threads be kept under tension during the spinning operation. The yarn is of pleasing appearance and feel. It is not affected by acids and alkalis and is not attacked by bacteria. The main disadvantage is the low softening point (150° F).¹⁹⁵

Although interpolymers made, for example, with equal proportions of vinyl chloride and vinyl acetate are apparently homogeneous, it has been shown by fractional precipitation that this is not the case, the ratio of the two components in individual fractions varying from 9:3 to 5:7. The most difficultly soluble products are richest in vinyl chloride.¹⁷⁰

Interpolymers with a minor amount of vinyl chloride have a lower softening point than the type discussed above, but have a higher softening point than polyvinyl acetate. They are colourless, transparent, light-fast, and dissolve readily in a wide range of lacquer solvents such as toluene and butyl acetate. Films are hard, tough, and when suitably formulated are durable; water resistance is moderate. Although the products are compatible with nitrocellulose, they are not miscible with drying oils or varnish diluents.¹³²

The interpolymers of vinyl chloride and acrylic and methacrylic esters are produced by mixing together the components and polymerizing in aqueous emulsion,¹⁹⁶ although it is said that better results are obtained by adding progressively the faster polymerizing acrylic ester to the slower polymerizing vinyl chloride as polymerization progresses.¹⁹⁷

These interpolymers containing a minor proportion of acrylic ester are broadly similar to corresponding vinyl acetate interpolymers. Compared with polyvinyl chloride they can be worked at a temperature of about 100° against 160–75°, which is an advantage where standard rubber machinery is involved. The interpolymers give films which are paler in colour and are more transparent, flexible, and elastic than the straight polymer.¹⁷¹

Other interpolymers deserving of mention are those produced with maleic and fumaric esters, which can be hydrolysed to alkali soluble products,¹⁹⁸ and with *asym.*-dichloroethylene, which possess desirable properties without requiring additional softening agents.¹⁹⁹

Miscellaneous Halogen Substituted Compounds.

Vinyl bromide polymerizes just as readily as vinyl chloride.²⁰⁰ The polymer is a white powder, insoluble in the common solvents.

Asym.-dichloroethylene $\text{CH}_2=\text{CCl}_2$, readily produced by treating 1:1:2-trichloroethane with milk of lime,²⁰¹ polymerizes more rapidly than vinyl chloride. Thus polymerization proceeds to the extent of 90 per cent. in the dark in 6 days, and is greatly accelerated by light.²⁰² The polymers so produced are white intractable powders, practically completely insoluble in organic solvents, and only softening at high

temperatures with decomposition. A wide range of interpolymers have been described.

Sym.-dichloroethylene $\text{ClCH}=\text{CHCl}$ shows very little disposition to polymerize.

Vinyl iodide is scarcely referred to in the literature, although it has been stated that it shows no marked tendency to polymerize;²⁰³ when exposed to ultra-violet light, it decomposes into acetylene and hydriodic acid.²⁰⁴

Allyl chloride $\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{Cl}$ polymerizes very slowly on exposure to ultra-violet light forming a low molecular weight polymer, obtained as a viscous syrup.²⁰⁵

Allyl bromide polymerizes even more slowly.

Vinyl Esters of Organic Acids.

Preparation. The most important organic vinyl esters are the acetate and the monochloroacetate. Other esters appear to have received comparatively little attention, although it is stated that they can be prepared by similar methods to the acetate.

Vinyl acetate is produced by the direct action of acetylene on acetic acid in the presence of a mercury catalyst.¹²⁸ The main problem has been to minimize the formation of ethylidene diacetate formed as a by-product. Since this undesirable side reaction is favoured by high temperatures, the main search has been for active catalysts giving high conversion to vinyl acetate at low temperatures. The following catalysts have been proposed with this in mind: mercury salts of acetyl-sulphuric acid,²⁰⁶ orthophosphoric acid,²⁰⁷ sulphoacetic acid²⁰⁸ and silicotungstic acid;²⁰⁹ boron fluoride alone²¹⁰ and in combination with hydrogen fluoride;²¹¹ ferric acetate;²¹² and methionic acid²¹³ which all show a promoting action when used in combination with a mercury catalyst. The reaction can also be carried out in the vapour phase using a zinc or cadmium acetate catalyst on active carbon, but the process does not compare favourably with the liquid-phase reaction (cf. ²¹⁴).

The process used at Shawinigan has been described in some detail.²¹⁵

Polymerization and Properties of Polymers.

The polymerization of vinyl acetate has been widely studied. Staudinger^{216, 217} has shown that polymers with an average molecular number of 20–100 can be produced by selecting appropriate conditions. In general, slow polymerization at low temperatures under the influence of ultra-violet light in an atmosphere of nitrogen gives the highest molecular weight polymers, whereas rapid polymerization at high temperatures in the presence of catalysts and solvents leads to low polymers. The influence of solvents is, however, somewhat variable. Thus, toluene, alcohol, chloroform, and acetone retard polymerization, the polymer remaining dissolved in the solvent. With petroleum ether, on the other hand, the polymer is pre-

cipitated as polymerization proceeds, and has a considerably greater molecular weight (cf. ²¹⁸).

A similar effect can be obtained by employing water and a water-miscible solvent at low temperatures, when the polymer is thrown out of solution. ²¹⁹ The amount of solvent present has a marked effect upon the properties of the resulting polymer. ²²⁰ The most favoured catalysts are peroxides, and in particular benzoyl peroxide, ¹²⁹ acetyl benzoyl peroxide, ²²¹ sodium peroxide, ²²² sodium perborate, ²²³ sodium perborate and acetic anhydride, which gives higher molecular weight products than benzoyl peroxide, ²²⁴ peroxides and acetic anhydride, ²²⁵ and ozone. ²²⁶ Other agents which have been proposed are lead tetraethyl, ²²⁷ silica gel, bauxite, and Florida earth. ²²⁸

The polymerization of vinyl acetate is highly exothermic, and may proceed with almost explosive violence. This has led to various proposals to control the process on the large scale. For example, vinyl acetate and catalyst is added slowly to a charge which is already polymerizing under reflux, partially polymerized material being continuously withdrawn, and the process completed in a second vessel. ²²⁹ A continuous method consists in introducing the monomer into the upper section of a long tube which is kept just below the boiling-point (73°) by cooling devices. The lower section where polymerization is well advanced is maintained at about 200° and the hot product is continuously ejected at the base on to a conveyor belt. ²³⁰ A convenient method consists in polymerizing to a syrupy consistency, emulsifying with water, and then completing the operation; ²³³ alternatively the monomer may be dispersed in water using a suitable dispersing agent such as polyvinyl alcohol and then polymerizing in this condition. ²³⁴

Acetaldehyde which is frequently present as an impurity influences polymerization; thus aldehyde free vinyl acetate does not polymerize at 100° in the presence of oxygen. ²³¹ Higher pressures increase the rate of polymerization; under very high pressures it is unnecessary to heat. ²³² In addition to phenols such as hydroquinone, copper or copper compounds ²³⁵ and sulphur ²³⁶ act as stabilizers, and permit of the distillation and storage of vinyl acetate without the consequence of uncontrolled polymerization. The properties of polyvinyl acetate depend upon the degree of polymerization. The low molecular weight polymers are comparatively brittle, and dissolve in a wide range of solvents forming solutions having low viscosity. As the molecular weight increases, the polymers become progressively tougher and harder, whilst solubility is diminished and viscosity increased. The highest polymers swell strongly in solvents and are difficult to dissolve, forming solutions of very high viscosity. The technical grades of polyvinyl acetate are colourless, transparent, light-fast, and tough, having s.g. 1.19; refractive index 1.467; dielectric strength (60-cycle) 1,000 volts per unit; tensile strength—5,000 lb. per sq. in; coefficient of linear expansion 0.000086 per $^{\circ}$ C.; water absorption (A.S.T.M.)—2.0; acid value—nil. On prolonged immersion about 8 per cent. water is absorbed and the polymers

become cloudy, but recover their transparency on drying. The polymers are thermoplastic, and soften at a comparatively low temperature. Thermal decomposition sets in at about 200°; vinyl acetate monomer is not regenerated. At moderate temperatures, the polymers become quite elastic and can be drawn into threads. Many solvents dissolve polyvinyl acetates including aromatic hydrocarbons, many esters, ketones, lower aliphatic alcohols and acids, and chlorinated hydrocarbons. The most important interpolymers of vinyl acetate are those obtained in conjunction with vinyl chloride which have already been discussed. In addition, vinyl esters can be interpolymerized with α - β -unsaturated carboxylic acids, and in particular maleic anhydride, by heating with a peroxide catalyst (cf. 237); the interpolymers are pale, transparent, and hard, and form alkali soluble salts.²³⁸ Acrylic acid may also be used.²³⁹ These aqueous solutions have been proposed as sizing agents for textiles,²⁴⁰ and for dyestuff lakes.²⁴¹ Vinyl acetate can be polymerized with di- and tri-chloroethylenes which do not polymerize readily alone, but in this case the products are viscous liquids which harden at ordinary temperatures.²⁴² By employing crotonic derivatives, products with a higher softening point, and improved water resistance are formed.²⁴³ Although polyvinyl acetate is incompatible with drying oils, mixed polymers of vinyl acetate with drying oils are homogeneous, and are suitable as varnish bases,²⁴⁴ compatible with nitrocellulose and the methyl, ethyl, and benzyl ethers of cellulose, but not with cellulose acetate or drying and non-drying oils. Although the polymer is not compatible with rosin, combination may be effected by heating to about 250°, when a partial polyvinyl ester of rosin is formed with elimination of acetic acid;²⁴⁵ the mixed ester is soluble in drying oils. In a similar manner, the acetate group may be replaced by other groups such as lactate or tartrate by heating with the appropriate acid.²⁴⁶

In general properties, polyvinyl chloroacetate compares fairly closely with polyvinyl acetate, but is not so widely compatible with cellulose derivatives. The chlorine atoms are capable of various replacement reactions. Thus treatment with pyridine gives a water-soluble base, useful in dyeing;²⁴⁷ whilst replacement may be effected with alkali compounds of organic acids, phenols, or alcohols.²⁴⁸

Applications. Although polyvinyl acetate has been advocated as a thermoplastic moulding composition, the low softening point greatly restricts applications in this field. By using it in combination with cellulose ethers²⁴⁹ and esters,²⁵⁰ more satisfactory moulding compositions have been produced. Sound records have been produced using amorphous silica as the filling agent.²⁵¹

The most important applications lie in the field of coating compositions on account of paleness in colour, light fastness, good ageing properties, good build, and wide range of solubility in cheap lacquer solvents. For many purposes, such as high-grade furniture and automobile lacquers, it is preferable to use these resins in combination with nitrocellulose. Without the addition of a small proportion of a cellulose derivative, the lacquer films tend to dry out rather slowly,

and to remain somewhat soft until the last traces of solvent disappear. In addition, lacquers based upon polyvinyl acetate have been proposed for wallpapers,²⁵² for waterproofing cellophane,²⁵³ as a basis of inks for intaglio printing,²⁵⁴ for stiffening toe caps of shoes,²⁵⁵ as coatings for leather,²⁵⁶ and as the basis of anti-rust paints.²⁵⁷ The products have been employed for the sizing of textiles;²⁵⁸ on scouring the tightly twisted yarn, crêpe effects are produced.²⁵⁹ Many uses in the general field of adhesives have been described—for example, as a general purpose adhesive when suitably plasticized,²⁶⁰ as a binding agent for abrasives,²⁶¹ for laminating sheets of cellulose derivatives,²⁶² as the inter-layering medium in safety glass, preferably in combination with a cellulose derivative,²⁶³ and for cementing glass to glass, and metal to metal.²⁶⁴

Polyvinyl Alcohol.

Polyvinyl alcohol is the product of complete hydrolysis of polyvinyl esters and is obtained by the action of either acid or alkali.^{265, 266} The usual source is polyvinyl acetate, although polyvinyl chloride under appropriate conditions will also serve.²⁶⁷ Acid hydrolysis is effected by refluxing in alcoholic solution with a little sulphuric acid, or by passing hydrogen chloride through the solution. Alkali hydrolysis may be brought about with an alkali metal hydroxide in the presence of alcohol; if sufficient water be present the polyvinyl alcohol does not separate during hydrolysis, but can be precipitated when this is complete by addition of alcohol.²⁶⁸ Ammonium hydroxide can also be used.²⁶⁹ Provided that an excess of alkali is employed, and the conditions are suitable, hydrolysis is complete; but with an amount of alkali insufficient to hydrolyse completely all the ester groupings, partially saponified polyvinyl esters can be produced having a wide range of properties according to the degree of hydrolysis. Polyvinyl alcohols carrying other groupings in the chain may be formed by hydrolysis of interpolymers of vinyl esters with other substances such as styrene, acrylic esters, and butadiene.^{270, 271}

Polyvinyl alcohol is a colourless or straw-coloured fibrous or granular opaque powder, insoluble in most organic solvents, but soluble in water. The properties are most influenced by the molecular weight of the parent ester. For technical purposes, polyvinyl alcohol from comparatively high molecular weight polyvinyl acetates seems to be preferred. Polyvinyl alcohol can readily be chlorinated,²⁷² the product so formed is stated to be valuable as a substitute for chromated albumen in lithography.²⁷³ Hydroxyalkyl and alkyl ethers are formed by interaction with an alkylene oxide.²⁷⁴ Polyvinyl alcohol is thermoplastic, and can be moulded and extruded to give somewhat flexible rods and tubes when suitably plasticized.²⁷⁵ The mouldings are chiefly valuable on account of their complete absence of swelling with oils and solvents, but suffer mainly from undue water sensitivity. Many attempts have been made to improve this feature, e.g. by heating to 160°, by treating with tannin or formaldehyde,²⁷⁶

polyacrylic acid,²⁷⁷ cuprammonium hydroxide solution,²⁷⁸ and certain iron and chromium compounds.²⁷⁹

Films and threads can be produced from solutions, preferably in aqueous alcohol;²⁸⁰ the threads are valuable as surgical sutures, particularly when admixed with a small amount of oxalic, malic, or lactic acids,²⁸¹ and the films have been applied to the manufacture of photographic films.²⁸² In the textile field, polyvinyl alcohol has been proposed as a sizing agent, either alone²⁸³ or in conjunction with oils, fats, and waxes,²⁸⁴ and as a dyestuff resist.²⁸⁵

Polyvinyl Acetals.

The polyvinyl acetals are a class of resins produced by the interaction of polyvinyl alcohol with aldehydes, of which the most important are formaldehyde (Formvar), acetaldehyde (Alvar), and *n*-butaldehyde (Butacite). The reaction is carried out at elevated temperatures in the presence of catalysts such as hydrochloric, sulphuric,²⁸⁶ and phosphoric²⁸⁷ acids, zinc chloride and aluminium chloride.²⁸⁸ Aldehydes differ in their reactivity; formaldehyde is the most reactive, followed by acetaldehyde, butaldehyde, and benzaldehyde. It is necessary to adjust the reaction conditions according to the nature of the reacting aldehyde and the degree of reaction desired. A more direct method of preparation avoids the preparation and isolation of polyvinyl alcohol as an intermediary by combining the polyvinyl ester, usually polyvinyl acetate, directly with the aldehyde.²⁸⁹ This can be effected in aqueous dispersion, the polyvinyl ester being dispersed with polyvinyl alcohol and the whole being reacted with the carbonyl compound.²⁹⁰ In addition to the aldehydes mentioned above, higher saturated aldehydes,²⁹¹ aldehydes (and also ketones) containing a primary, secondary, or tertiary group (for example, *p*-aminobenzaldehyde²⁹²), carboxylic acids containing a reactive carbonyl group (for example, malonic aldehyde²⁹³), mixtures containing at least one cyclic aldehyde,²⁹⁴ and mixtures of propionic aldehyde with another aldehyde having less than four carbon atoms,²⁹⁵ have all been described as giving especially valuable products. A convenient method of isolating the resins from the acid solutions consists in atomizing with ammonia gas into a large volume of vigorously agitated aqueous ammonia.²⁹⁶

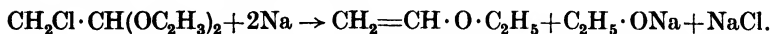
The properties of the polyvinyl acetals vary widely according to the molecular weight of the parent polyvinyl ester, the nature of the substituent group, and the degree of replacement. In the case of formaldehyde, replacement progressively leads to an increase in softening point, hardness and toughness, and reduction in solubility. In these respects the changes are more marked than for a corresponding replacement with acetaldehyde. The products are colourless, odourless, tasteless, and of good water resistance. The rate of moisture transmission is above $\frac{1}{10}$ that of regenerated cellulose, and $\frac{1}{4}$ that of cellulose acetate. Products of high replacement are soluble only in dioxan, acetic acid, and a few chlorinated solvents. Films

are hard, tough, light-fast, and of great mechanical strength and flexibility. Softening point is so high that they must be plasticized before they can be used for moulding. Polyethylene glycol hexoate,^{297, 298} diethylene glycol dipropionate,²⁹⁹ and a mixture of diphenyl ether and a lower dialkyl phthalate³⁰⁰ are particularly valuable plasticizing agents for use with this class of resin. With acetaldehyde, about 95 per cent. replacement is possible without affecting the solubility and compatibility characteristics. At 70–80 per cent. replacement the softening point is raised by about 50°, and the solution viscosity is doubled. As lacquer resins, these products are superior to polyvinyl acetate in respect of the greater hardness and toughness, and superior adhesion. They are used either alone as spirit varnishes, or in conjunction with nitrocellulose. The high tensile strength and softening point renders these products suitable for thermoplastic moulding compositions, and for the production of sheets, rods, tubes, and general mouldings. High-grade gramophone records have been made in admixture with suitable fillers and lubricants.³⁰¹ In the spinning of fibres of the viscose type, enhanced gloss, durability, and softness is imparted by adding a proportion of a polyvinyl acetal to the solution to be spun.^{302, 303}

Polyvinyl butyral is even lower softening than the parent ester from which it is formed. At ordinary temperatures, it is flexible, extremely tough, and recovers fairly quickly after being stretched. These properties are accentuated by additions of comparatively small amounts of plasticizer, and the lightly plasticized compositions are somewhat rubber-like. Plasticized polyvinyl butyral has achieved notable interest as an interlayer for laminated safety glass on account of its great film strength, excellent adhesion, transparency and light fastness, and lack of brittleness at low temperatures.

VINYL ETHERS

Vinyl ethyl ether was first prepared by Wislicenus³⁰⁴ by treating chloroacetal with metallic sodium.



This was simplified later by Claisen³⁰⁵ by reacting diethyl acetal with phosphorus pentoxide in quinoline, when alcohol is removed. This reaction may be effected in the vapour phase, under the catalytic effect of silver and other finely divided metals,³⁰⁶ and is applicable to many vinyl ethers.

Halogen substituted olefines on treatment with sodium or potassium alkoxides afford the corresponding vinyl ether; thus Geuther³⁰⁷ obtained dichlorovinylethyl ether by treating *asym.*-tetrachloroethane with sodium ethylate.

Trichloroethylene can similarly be used.³⁰⁸ The simplest example is vinyl chloride which affords vinyl alkyl or aryl ethers according to the alcohol or phenol employed.³⁰⁹

Halogen substituted alkyl ethers when treated with alkoxides or concentrated alkali give the corresponding vinyl ethers.³¹⁰

The most direct method of preparation consists in combining acetylene with alcohols or phenols at high temperatures under pressure in the presence of alkaline catalysts.³¹¹ This reaction is of a general character, and has been employed for preparing a wide variety of vinyl ethers.

Vinyl ethers do not polymerize as readily as most vinyl compounds. Thus, the mass or homogeneous method of polymerization employing heat and peroxide catalysts is either ineffective or leads to the formation of low molecular weight polymers which are soft and of a balsam-like nature. Iodine³¹⁰ and sulphur dioxide³¹² are rather more effective than peroxides. Emulsion methods have been described, but it is apparently necessary to conduct the operation under alkaline or neutral conditions.³¹³

The interpolymerization of vinyl ethers with other vinyl compounds such as vinyl esters and acrylic derivatives leads to interpolymers having a wide variety of properties according to the nature of the components.³¹³ Interpolymerization of vinyl ethers with maleic anhydride and ethylene dicarboxylic acid derivatives proceeds readily.³¹⁴ Products of this type are claimed to be useful for textile applications as sizing and dyeing assistants, adhesives, and bases for lacquers.

VINYL KETONES

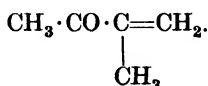
The vinyl ketones were first studied in some detail by Blaise and Maire,³¹⁵ who prepared a series by heating the corresponding alkyl β -chloroethyl ketones with diethylaniline. Methyl β -chloroethyl ketone is obtained by interaction between acetyl chloride and ethylene;³¹⁶ under appropriate conditions this is not isolated, the reaction proceeding directly to vinyl methyl ketone in the presence of aluminium chloride.³¹⁷



A further method consists in condensing acetone with formaldehyde under carefully regulated conditions, and then dehydrating the so-formed methyl β -hydroxyethyl ketone with zinc chloride.³¹⁸



In a similar manner methyl ethyl ketone affords isopropenyl methyl ketone³¹⁹



An attractive synthesis of vinyl methyl ketone is based upon the hydration of monovinyl acetylene, an intermediate in the manufacture of 2-chloro-1:3-butadiene (chloroprene) used for making

synthetic rubbers (Neoprene). In the presence of a mercury catalyst, hydration occurs readily.³²⁰⁻³



Polymerization is effected in the usual manner with oxygen and oxygen evolving agents.³²⁴ It is, however, necessary not to resort to high temperatures owing to dimerization leading to 1-octene-3-7-dione.³²⁵



Under aqueous conditions at high temperature the corresponding hydrated ketone, 1-hydroxy-octane-3-7-dione is formed. Polymerization appears to proceed rather more slowly than most vinyl compounds. Isopropenyl methyl ketone polymerizes slowly at room temperature under nitrogen, forming a tough, hard, colourless, glass-like mass soluble in organic solvents.^{326, 327}

UNSATURATED ALDEHYDES

From the present viewpoint, *acrolein* is the most important and interesting of the unsaturated aldehydes. Various methods for preparing acrolein from glycerol have been described involving the use of potassium bisulphate and potassium sulphate,³²⁸ metallic oxides,³²⁹ zinc sulphate,³³⁰ kieselguhr,³³¹ and certain metallic phosphates.³³² It is also formed under appropriate conditions by condensation of acetaldehyde and formaldehyde.³³³

Acrolein polymerizes exceptionally readily; Moureu³³⁴ has shown that it responds particularly strongly to the influence of light, to very small amounts of oxygen, and to heat. Conditions appear to be somewhat critical; for example, substantial amounts of oxygen inhibit the reaction, whilst light and oxygen in low concentrations are not as might be anticipated mutually complementary, but tend to inhibit. Aqueous solutions of acrolein are polymerized with great rapidity by the action of alkaline reacting substances such as potassium carbonate.³³⁵ By variations in the nature and concentration of alkali, polymers with varying solubility characteristics are formed.³³⁶ The polymer separates from solution as a colourless powder as polymerization proceeds. Methods have been described for controlling the polymerization to give more soluble products which involve the use of moderators such as salts of heavy metals.³³⁷ Acrolein is stabilized by phenols and amines.

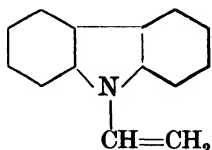
Acrolein polymer produced under drastic conditions is insoluble in most organic solvents with the exception of hot alcohol. By regulating polymerization along the lines indicated, polymers are obtained which dissolve also in ketones and organic acids.

Acrolein polymers are by comparison with other vinyl polymers, comparatively unstable. Thus, decomposition occurs on heating with dilute acids or alkalis. The products are more or less thermoplastic

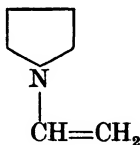
according to the method of preparation, but decompose at fairly low temperatures.

N-VINYL POLYMERS

The N-vinyl polymers are of comparatively recent development. Principal interest has so far been confined to *N*-vinyl carbazole



Crude anthracene from coal tar contains a high proportion of carbazole which serves as the starting material. It readily forms compounds with alkali metals. This provides a method for separation and purification, and can at the same time be utilized for conversion to N-vinyl carbazole by interacting the alkali metal salt (e.g. potassium carbazole) with vinyl chloride in an inert solvent.³³⁸ Further methods consist in interacting carbazole with acetylene in the presence of alkali catalysts at moderate temperatures under pressure,³³⁹ and also by a vapour-phase modification in which carbazole and acetylene are passed at high temperatures over alkaline catalysts.³⁴⁰ Other N-vinyl compounds such as *N*-vinyl pyrrole



are formed under somewhat similar conditions.

These compounds polymerize by the general methods already discussed, in solution or in aqueous emulsion, accelerated by organic peroxides and acid-reacting catalysts such as boron fluoride and zinc chloride. Interpolymers can be produced by interpolymerizing with a wide range of other unsaturated compounds such as styrene.³⁴¹

The outstanding feature of N-vinyl carbazole polymers is their high softening point (250°), and in this respect they are unique amongst the thermoplastic polymers. The polymers are transparent, pale in colour, and very hard. The mechanical properties of the polymerides can be improved by extrusion or hot rolling, which orient the molecules.³⁴² The polymers are lacking in flexibility, and benefit from plasticization; thus, chlorinated naphthalene and chlorinated diphenyl are employed in compositions for electrical uses.³⁴³ Another method is to blend with a softening agent, subject the plastic simultaneously to transverse and longitudinal tension, and immerse while still under tension in a solvent for the softening agent.³⁴⁴ The resulting dried film is found to have lost its brittleness.

N-vinyl carbazole polymer is produced commercially under the name 'Luvican'.

The results of the investigation of the conditions of polymerization of styrene and vinyl materials will be discussed in the chapter on the 'Problems of Resinification', pp. 433-4.

REFERENCES

1. *Farben-Ztg.*, 1929, **34**, 837.
2. I.G., B.P. 293,487; B.P. 313,067; B., 1929, 671. B.P. 326,322; B., 1930, 500.
3. I.G., B.P. 340,573; B., 1931, 358.
4. N.V. de Baat. Petrol., B.P. 358,068; B., 1932, 172.
5. I.G., B.P. 336,234; B., 1931, 10.
6. V. N. Ipatiev, *Ber.*, 1913, **46**, 1748.
7. Allen, *J. Phys. Chem.*, 1932, **36**, 1601.
8. V. N. Ipatiev, *Ber.*, 1911, **44**, 2978.
9. I.C.I., B.P. 471,590; B., 1937, 1309.
10. I.C.I., B.P. 474,426; B., 1938, 942.
11. I.C.I., B.P. 499,333; B., 1939, 237.
12. I.C.I., B.P. 472,051; B., 1938, 635.
13. I.C.I., B.P. 497,643; B., 1939, 240.
14. I.C.I., B.P. 481,515; B., 1938, 625.
15. I.C.I., B.P. 505,761; B., 1939, 959.
16. N.V. de Baat. Petrol., F.P. 823,345.
17. I.G., B.P. 478,003; B., 1938, 252.
18. Usines de Melle, B.P. 522,818; B., 1940, 725.
19. I.G., F.P. 853,642.
20. I.G., B.P. 401,297; B., 1934, 136.
21. Standard Oil Development Co. Ltd., B.P. 505,736; B., 1939, 804.
22. Standard Oil Development Co. Ltd., B.P. 509,463; B., 1939, 1021.
23. I.G., B.P. 525,542.
24. U.S. Rubber Prod., B.P. 511,041; B., 1939, 1135.
25. Elect. Res. Prod., B.P. 490,147.
26. I.G., B.P. 434,266; B., 1935, 1059.
27. I.G., G.P. 676,909.
28. Standard Oil Development Co. Ltd., U.S.P. 2,160,996
29. Standard Oil Development Co. Ltd., F.P. 852,861.
30. Standard Oil Development Co. Ltd., B.P. 511,418; B., 1939, 1099.
31. Standard Oil Development Co. Ltd., B.P. Appl. 31,461/39.
32. Bonastre, *J. de Pharm.*, 1831, **17**, 338.
33. Gerhardt and Cahours, *Ann.*, 1841, **38**, 325.
34. Hempel, *Ann.*, 1846, **59**, 318.
35. Fittig and Binder, *Ann.*, 1878, **195**, 137.
36. I. Ostromislenski, U.S.P. 1,541,176.
37. S. Sabetay, *Bull. Soc. Chim.*, 1929, **45**, 69.
38. Klages and Allendorf, *Ber.*, 1898, **31**, 1003, 1298.
39. I.G., B.P. 338,262; B., 1931, 238.
40. S. Natelson, *Ind. Eng. Chem.*, 1933, **25**, 1391; Dow Chemical Company, U.S.P. 2,225, 543.
41. A.P.V.M. Circ. 410, 162.
42. I. Ostromislenski and M. G. Sheppard, U.S.P. 1,552,875.
43. I.G., B.P. 340,587; B., 1931, 335.
44. I.G., B.P. 371,587; B., 1932, 587.
45. I.G., G.P. 560,686.
46. O. H. Smith, U.S.P. 1,687,903; B., 1929, 511.
47. I.G., G.P. 559,737.
48. DuPont de Nemours & Co., U.S.P. 1,892,386.
49. G. W. Jargstoffs, U.S.P. 1,870,832.
50. I.G., G.P. 590,166.
51. O. H. Smith, U.S.P. 1,870,878.
52. Consort. f. Elekt. Chem. Ind., B.P. 508,666; B., 1939, 916.
53. Simon, *Ann.*, 1839, **31**, 267.
54. Blyth and Hofmann, *Ann.*, 1845, **53**, 314.
55. Lemoine, *Compt. Rend.*, 1897, **125**, 530.
56. Kronstein, *Ber.*, 1902, **35**, 4153.
57. Stobbe and Posnjak, *Ann.*, 1909, **371**, 270.
58. H. Stobbe, *Ann.*, 1915, **409**, 1.
59. H. Staudinger, *Die hochmol. org. Verbind.* (Springer, Berlin, 1932, 186.)
60. I. Ostromislenski, U.S.P. 1,683,403.
61. I. Ostromislenski and M. G. Sheppard, U.S.P. 1,541,173; B., 1925, 692.
62. N. Milas, *Proc. Nat. Acad. Sci.*, 1928, **14**, 844.
63. S. Natelson, *Ind. Eng. Chem.*, 1933, **25**, 1391.
64. I.G., B.P. 355,573; B., 1932, 57.
65. B. O. Houtz and H. Adkins, *J. Amer. Chem. Soc.*, 1931, **53**, 1058.
66. DuPont de Nemours & Co., B.P. 319,587; B., 1931, 666.
67. Boeseken and Bastit, *Rec. trav. chim.*, 1913, **32**, 191.
68. Wieland and Dirren, *Ber.*, 1930, **63**, 404.

69. H. Staudinger and H. A. Bruson, *Ann.*, 1926, **447**, 115.
70. H. Staudinger and M. Brunner, *Helv. Chim. Acta*, 1929, **12**, 950.
71. K. Fredenhagen, G.P. 524,220.
72. K. Ziegler and H. Kleiner, *Ann.*, 1929, **473**, 57.
73. I.G., B.P. 340,004; B., 1931, 333.
74. Young and Douglas, U.S.P. 1,775,882.
75. Res. Prod. Chem. Co., U.S.P. 1,892,101.
76. Brit. Cel., B.P. 409,132; B., 1934, 534.
77. Punmerer, G.P. 576,141.
78. DuPont de Nemours & Co., B.P. 319,590.
79. O. H. Smith, B.P. 355,790; B., 1932, 72.
80. J. W. Breitenbach, *Öst. Chem.-Ztg.*, 1938, **41**, 182.
81. G. Tammann and W. Pape, *Z. anorg. Chem.*, 1931, **200**, 113.
82. DuPont de Nemours & Co., U.S.P. 1,952,116; B., 1935, 139.
83. I. Ostromislenski, B.P. 233,649; B., 1926, 451.
84. I.G., B.P. 365,217; B., 1932, 519.
85. Korshavlu, *J. Appl. Chem. Russia*, 1938, **11**, 853.
86. T. Wagner-Jauregg, *Ber.*, 1930, **63**, 3213.
87. I.G., H.P. 376,479; B., 1932, 948.
88. H. Staudinger and W. Heuer, *Kaut.*, 1934, **10**, 7.
89. I.G., G.P. 653,083.
90. I.G., B.P. 339,255; B., 1931, 264.
91. I.G., B.P. 313,569; B., 1930, 1121.
92. I.G., B.P. 357,173; B., 1931, 1107.
93. I.G., B.P. 371,396; B., 1932, 688.
94. I.G., B.P. 399,232; B., 1933, 1069.
95. I. Ostromislenski, U.S.P. 1,613,674.
96. I. Ostromislenski, U.S.P. 1,705,204; B., 1929, 746.
97. I.G., B.P. 345,197; B., 1931, 508.
98. I. Ostromislenski, U.S.P. 1,613,673.
99. DuPont de Nemours & Co., B.P. 392,924; B., 1933, 639.
100. A. J. Weith and others, *Ind. Eng. Chem.*, 1940, **32**, 1301.
101. H. A. Gardner, Amer. Paint & Var. Man. Assoc., (irc. 410 (1932).
102. DuPont de Nemours & Co., B.P. 311,700; B., 1930, 872.
103. Selden Co., U.S.P. 1,941,474.
104. I.G., B.P. 375,330.
105. Celluloid Corp., B.P. 402,877; B., 1934, 189.
106. DuPont de Nemours & Co., B.P. 315,288.
107. Internat. Gen. Elect. Co., B.P. 401,500; B., 1934, 157.
108. Norddeuts. Seckabelwerke, A. G., B.P. 414,527; B., 1934, 898.
109. I.G., B.P. 367,126; B., 1932, 418.
110. Cellon-Werke, Dr. A. Eichengrün, B.P. 373,995; B., 1932, 779.
111. Allgem. Elekt. Ges., G.P. 598,279.
112. Horn, *Kunst.*, 1940, **30**, 53.
113. H. Staudinger, *Ber.*, 1929, **62**, 263.
114. H. Staudinger, *Ber.*, 1929, **62**, 2406.
115. I.G., F.P. 760,861.
116. I.G., B.P. 367,416; B., 1932, 591.
117. DuPont de Nemours & Co., B.P. 364,873; B., 1932, 494.
118. H. Staudinger, *Ber.*, 1929, **62**, 442.
119. Distillers Co., B.P. 506,160.
120. H. Staudinger and Dreher, *Ann.*, 1935, **517**, 73.
121. L. Palfray, S. Sebetyay, and D. Sontag, *Compt. rend.*, 1932, **194**, 2065; A., 1932, 839.
122. Regnault, *Ann.*, 1835, **14**, 28, 34.
123. Baumann, *Ann.*, 1872, **163**, 317.
124. I. Ostromislenski, B.P. 6,299/1912.
125. I. Ostromislenski, *J. Russ. Chem. Soc.*, 1916, **48**, 1114.
126. J. Plotnikov, *Chem. Zentr.*, 1922, **1**, 940.
127. G. Flumiani, *Koll.-Z.*, 1928, **45**, 152.
128. Chem. Fabrik. Griess-Elektron., B.P. 14,246, 1913.
129. Chem. Fabrik. Griess-Elektron., B.P. 15,271, 1915.
130. *Farben-Ztg.*, 1929, **34**, 837.
131. G. O. Morrison and T. Shaw, *Chem. Met. Eng.*, 1933, **40**, 293.
132. Carbide and Carbon Chemicals Corp., B.P. 255,049; B., 1929, 219.
133. Chem. Fabrik (vorm. E. Schering), G.P. 278,240.
134. Consort. f. Elektrochem. Ind., B.P. 339,093; B., 1931, 289.
135. I.G., B.P. 402,980.
136. I.G., B.P. 339,727; B., 1931, 334.
137. I.C.I., B.P. 349,017; B., 1931, 875.
138. J. van Dalsen and J. P. Wibaut, *Rec. trav. chim.*, 1934, **53**, 489.
139. Plauson, B.P. 156,120.
140. Carbide and Carbon Chem. Corp., U.S.P. 1,934,324; B., 1934, 873.
141. Carbide and Carbon Chem. Corp., U.S.P. 1,752,049.
142. P. Pavlovitsch, *Ind. Org. Chem.*, U.S.S.R., 1936, **2**, 127
143. I.G., B.P. 349,263; B., 1931, 917.
144. Biltz, *Ber.*, 1903, **35**, 3524.
145. Senderens, *Compt. rend.*, 1908, **146**, 1213.
146. I.G., G.P. 585,793.
147. Van Dyke, B.P. 255,837.
148. H. Staudinger, M. Brunner, and W. Feist, *Helv. Chim. Acta*, 1930, **13**, 805.
149. I.G., B.P. 385,004; B., 1933, 182.

150. DuPont de Nemours & Co., U.S.P. 1,874,107.
151. Carbide and Carbon Chem. Corp., B.P. 408,338; B., 1934, 371.
152. P. Pavlovitch, *J. Appl. Chem. Russ.*, 1937, 10, 1071; B., 1937, 1237.
153. I.G., B.P. 410,132; B., 1934, 638.
154. I.G., B.P. 482,583; B., 1938, 764.
155. I.G., B.P. 482,647; B., 1938, 764.
156. Goodrich Co. and W. L. Semon, B.P. 398,091; B., 1933, 930.
157. S. L. Brous and W. L. Semon, *Ind. Eng. Chem.*, 1935, 27, 667.
158. I.G., B.P. 478,965; B., 1938, 1194.
159. I.G., B.P. 500,298; B., 1939, 630.
160. I.G., B.P. 480,592; B., 1938, 1331.
161. I.G., B.P. 478,616; B., 1938, 689.
162. Brit. Thomson-Houston Co., B.P. 499,931; B., 1939, 636.
163. Deuts. Celluloid-Fabrik, B.P. 451,675; B., 1936, 1007.
164. I.G., B.P. 467,167; B., 1937, 946.
165. I.G., B.P. 418,230; B., 1935, 13.
166. I.G., B.P. 336,237; B., 1931, 73.
167. I.G., B.P. 454,232; B., 1936, 1218.
168. Carbide and Carbon Chem. Corp., B.P. 451,723; B., 1936, 1007.
169. Carbide and Carbon Chem. Corp., B.P. 497,879; B., 1939, 295.
170. H. Staudinger and J. Schneiders, *Ann.*, 1939, 541, 151.
171. Chevassus, *Rev. gen. mat. plast.*, 1938, 298.
172. I.G., B.P. 387,976; B., 1933, 301.
173. I.G., B.P. 479,202; B., 1938, 1192.
174. I.G., B.P. 504,450.
175. *Chem. Age*, 1939, 40, 169.
176. Jentgen, *Kunstseide*, 1939, 21, 123.
177. Schmidt, B.P. 443,855.
178. Hamilton, *I.R.I.*, 1938, 7, 14.
179. I.G., B.P. 428,873; B., 1935, 670.
180. Deuts. Celluloid-Fabrik, B.P. 470,969; B., 1938, 157.
181. Deuts. Aktien Ges., B.P. 429,316.
182. I.G., B.P. 437,586.
183. Deuts. Celluloid-Fabrik, B.P. 440,887; B., 1936, 276.
184. Dynamit, A.G., H.P. 469,090.
185. I.G., B.P. 401,200; B., 1934, 29.
186. I.G., B.P. 485,115; B., 1938, 1331.
187. I.G., B.P. 423,568; B., 1935, 382.
188. I.G., B.P. 425,181; B., 1935, 406.
189. I.G., B.P. 432,977; B., 1935, 963.
190. I.G., B.P. 435,864; B., 1935, 1154.
191. Carbide and Carbon Chem. Corp., B.P. 388,309; B., 1933, 357.
192. Carbide and Carbon Chem. Corp., B.P. Appl. 25,194/38.
193. J. G. Davidson and H. B. McClure, *Ind. Eng. Chem.*, 1933, 25, 645.
194. Carbide and Carbon Chem. Corp., U.S.P. 1,990,903; B., 1936, 110.
195. *Textile Record*, 1940, 58, 33.
196. I.G., B.P. 358,534.
197. I.G., B.P. 467,084; B., 1937, 946.
198. I.G., B.P. 476,727; B., 1938, 300.
199. I.G., B.P. 477,532; B., 1938, 533.
200. Loew, *Ber.*, 1878, 11, 1258.
201. I.G., B.P. 349,872; B., 1931, 917.
202. H. Staudinger and W. Feist, *Helv. Chim. Acta*, 1930, 13, 832.
203. J. Spence, *J. Amer. Chem. Soc.*, 1933, 55, 1290.
204. G. Emschwiller, *Compt. rend.*, 1934, 199, 464.
205. H. Staudinger and T. Fleitmann, *Ann.*, 1930, 480, 92.
206. Canadian Electro Products Co. Ltd., B.P. 308,169; B., 1931, 12.
207. Canadian Electro Products Co. Ltd., U.S.P. 1,710,107.
208. Carbide and Carbon Chem. Corp., B.P. 490,334; B., 1938, 1267.
209. I.C.I., B.P. 351,318; B., 1931, 1003.
210. I.G., G.P. 582,544.
211. I.G., G.P. 604,640.
212. DuPont de Nemours & Co., B.P. 379,705; B., 1932, 1114.
213. Boehringer and Soehne, F.P. 770,154.
214. S. N. Ushakov and J. M. Feinstein, *Ind. Eng. Chem.*, 1934, 26, 501.
215. G. O. Morrison and T. Shaw, *Chem. Trade Journ.*, 1933, 92, 415.
216. H. Staudinger, *Ber.*, 1927, 60, 1782.
217. H. Staudinger and A. Schwalbach, *Ann.*, 1931, 488, 8.
218. I.C.I., B.P. 366,892.
219. I.G., B.P. 319,682; B., 1930, 1015.
220. Canad. Electro-Prod., B.P. 387,353; B., 1933, 296.
221. Carbide and Carbon Chem. Corp., B.P. 397,364; B., 1933, 886.
222. Canad. Electro Prod., B.P. 387,323; B., 1933, 296.
223. Canad. Electro Prod., B.P. 387,335; B., 1933, 296.
224. I.G., B.P. 337,806; B., 1931, 170.
225. I.G., F.P. 706,593.
226. DuPont de Nemours & Co., B.P. 319,587; B., 1931, 666.
227. Carbide and Carbon Chem. Corp., U.S.P. 1,775,882.
228. *Gen. Chem. Met.*, 1932, 16, 252.
229. Consort. f. Elektrochem. Ind., U.S.P. 1,710,825; B., 1929, 512.
230. I.G., B.P. 381,693; B., 1933, 168.

231. A. C. Cuthbertson, G. Gee, and E. K. Rideal, *Nature*, 1937, **140**, 889.
232. G. Tamman and W. Pape, *Z. anorg. Chem.*, 1931, **200**, 113.
233. I.G., G.P. 506,148.
234. I.C.I., B.P. 444,257; B., 1936, 705.
235. I.G., G.P. 503,919.
236. Canad. Electro Products, U.S.P. 1,768,434.
237. R. S. Morrell and H. Samuels, *J. Chem. Soc.*, 1932, 2215.
238. I.G., B.P. 376,479; B., 1932, 948.
239. I.G., F.P. 718,277.
240. I.G., G.P. 571,665.
241. I.G., B.P. 359,643; B., 1932, 222.
242. Consort. f. Elektrochem. Ind., G.P. 550,883.
243. I.G., B.P. 495,337; B., 1939, 405.
244. Consort. f. Elektrochem. Ind., B.P. 367,102; B., 1932, 437.
245. I.G., G.P. 506,148.
246. H. Dreyfus, B.P. 385,978; B., 1933, 217.
247. I.G., G.P. 542,778.
248. DuPont de Nemours & Co., B.P. 364,400; B., 1932, 272.
249. Celluloid Corp., B.P. 308,658; B., 1930, 1146.
250. Celluloid Corp., B.P. 335,582.
251. United Research Corp., U.S.P. 1,946,597; B., 1934, 1071.
252. I.G., B.P. 344,113.
253. DuPont de Nemours & Co., B.P. 380,483; B., 1932, 1041.
254. I.G., B.P. 307,3877.
255. Consort. f. Elektrochem. Ind., B.P. 314,541.
256. Soc. Door and Hoffmann, B.P. 369,260; B., 1932, 475.
257. Consort. f. Elektrochem. Ind., B.P. 314,499; B., 1931, 170.
258. Brit. Celanese, B.P. 346,267; B., 1931, 674.
259. H. Dreyfus, B.P. 352,451; B., 1931, 880.
260. Rohm and Haas, B.P. 373,947; B., 1932, 722.
261. I.G., B.P. 363,676.
262. Brit. Celanese Ltd., B.P. 354,280.
263. *Chem. Age*, 1932, **27**, 472.
264. F. Ohl, *Chem. Abs.*, 1934, **28**, 7437.
265. W. O. Herrmann and W. Haehnel, *Ber.*, 1927, **60**, 1658.
266. Consort. f. Elektrochem. Ind., U.S.P. 1,672,156.
267. Consort. f. Elektrochem. Ind., G.P. 516,996.
268. Eastman Kodak Co., U.S.P. 1,897,856; B., 1933, 954.
269. I.G., G.P. 575,780.
270. I.G., F.P. 697,693.
271. I.G., F.P. 724,910.
272. Harris-Seybold-Potter Co., B.P. 499,057.
273. Harris-Seybold-Potter Co., B.P. 501,069; B., 1939, 637.
274. Consort. f. Elektrochem. Ind., G.P. 591,979.
275. I.G., B.P. 505,651.
276. I.G., G.P. 526,497.
277. I.G., B.P. 487,056; B., 1939, 176.
278. DuPont de Nemours & Co., U.S.P. 2,130,212.
279. Chem. Forschungsges., B.P. 476,426; B., 1938, 1077.
280. Consort. f. Elektrochem. Ind., B.P. 393,505; B., 1933, 677.
281. Consort. f. Elektrochem. Ind., B.P. 420,052; B., 1935, 112.
282. S. E. Sheppard and J. G. McNally, U.S.P. 1,768,795; B., 1931, 276.
283. I.G., U.S.P. 1,920,564.
284. I.G., B.P. 345,207; B., 1931, 535.
285. I.G., B.P. 355,059; B., 1932, 19.
286. Zelger, F.P. 769,011.
287. I.G., B.P. 356,408; B., 1932, 95.
288. I.G., U.S.P. 1,955,068.
289. Bellore, U.S.P. 1,990,399.
290. I.G., B.P. 482,210; B., 1938, 625.
291. Shawinigan Chemicals Co. Ltd., B.P. 465,873; B., 1937, 1373.
292. I.G., B.P. 509,012; B., 1939, 918.
293. I.G., B.P. 510,168; B., 1939, 1024.
294. Eastman Kodak Co., B.P. 483,223; B., 1938, 943.
295. Eastman Kodak Co., B.P. 483,222; B., 1938, 943.
296. I.C.I., B.P. 498,396; B., 1939, 633.
297. Carbide and Carbon Chem. Corp., B.P. 497,737; B., 1939, 294.
298. Carbide and Carbon Chem. Corp., B.P. 497,739; B., 1939, 294.
299. Fiberloid Corp., U.S.P. 2,070,331; B., 1939, 630.
300. Eastman Kodak Co., U.S.P. 2,138,339.
301. Shawinigan Chemicals Co. Ltd., B.P. 410,770.
302. I.G., B.P. 372,647; B., 1932, 721.
303. I.G., B.P. 367,274; B., 1932, 417.
304. Wislicenus, *Ann.*, 1878, **192**, 106.
305. L. Claisen, *Ber.*, 1898, **31**, 1019.
306. I.G., B.P. 345,253; B., 1931, 667.
307. Geuther and Brockhoff, *J. pr. Chem.*, 1873, **7**, 112.
308. Consort. f. Elektrochem. Ind., B.P. 5,014/07.
309. I.G., B.P. 332,605.
310. Chalmers, *Can. J. Res.*, 1932, **7**, 464.
311. I.G., B.P. 369,297; B., 1932, 670.

312. I.G., B.P. 443,978; B., 1936, 654.
313. I.G., B.P. 373,343; B., 1932, 851.
314. I.G., B.P. 376,481; B., 1932, 948.
315. Blaise and Malre, *Bull. Soc. Chim.*, 1908, 3 (4), 165.
316. Kraplwin, *Chem. Zentr.*, 1910, 1, 1335.
317. Kraplwin, *Chem. Abs.*, 1911, 5, 1281.
318. Bayer, B.P. 19,088/00.
319. Morgan, Megson, and Pepper, *Chem. and Ind.*, 1938, 885.
320. DuPont de Nemours & Co., B.P. 388,402; B., 1933, 379.
321. I.G., B.P. 499,034; B., 1939, 355.
322. I.G., B.P. 502,813; B., 1939, 579.
323. I.G., B.P. 508,080; B., 1939, 915.
324. I.G., G.P. 568,907.
325. F. Bayer & Co., G.P. 227,176.
326. H. Staudinger, *Ber.*, 1934, 67, 1773.
327. K. W. Pepper, *Br. Plastics*, 1939, 10, 609.
328. C. Moureu, B.P. 141,057.
329. F. H. Constable, *Proc. Roy. Soc.*, 1926, 113A, 254.
330. G. Brus, *Bull. Soc. Chim.*, 1923 (4), 33, 1438.
331. Chem. Fabrik Aktien, G.P. 451,535.
332. Schering-Kahlbaum, A.G., B.P. 346,221; B., 1931, 710.
333. A. Stepanow and M. Schtschukina, *Zentr.*, 1927, 1, 1167; A., 1927, 647.
334. C. Moureu, *Compt. Rend.*, 1924, 179, 1229.
335. R. McLeod, *Amer. Chem. J.*, 1907, 37, 20.
336. C. Moureu, B.P. 141,085.
337. C. Moureu, B.P. 141,058.
338. I.G., B.P. 470,077; B., 1937, 1179.
339. I.G., G.P. 618,120.
340. I.G., B.P. 470,116; B., 1937, 1179.
341. I.G., G.P. 664,231.
342. I.G., B.P. 464,806; B., 1937, 1230.
343. I.G., F.P. 830,850.
344. I.G., B.P. 519,788; B., 1940, 468.

CHAPTER VI
ACRYLIC ACID RESINS

By ROWLAND HILL

THE acrylic resins comprise products obtained by the polymerization of acrylic acid $\text{CH}_2=\text{CH}\cdot\text{COOH}$ and derivatives thereof, for example, esters, amides, and nitriles, together with simple functional derivatives such as α -methyl acrylic acid $\text{CH}_2=\text{C}(\text{CH}_3)\cdot\text{COOH}$, commonly referred to as methacrylic acid. The facility with which these compounds undergo polymerization is closely influenced by the state of conjugation. When this no longer exists, as in vinyl acetic acid $\text{CH}_2=\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$, there is virtually no disposition displayed for polymerization. The position of the substituent grouping in functional derivatives of acrylic acid also plays an important role in this connexion. β -Substitution detracts from polymerization; thus crotonic derivatives, e.g. $\text{CH}_3\cdot\text{CH}=\text{CH}\cdot\text{COOH}$, are relatively stable to polymerization influences when compared with the corresponding methacrylic derivatives. On the other hand, the particular form of the grouping in acrylic and methacrylic derivatives does not appear to have a notable effect on their capacity to undergo polymerization; there is no marked divergence in behaviour between various esters, amides, and nitriles.

Historical.

The facility with which this class of compound undergoes polymerization has been recognized for many years. The original observations were made by early workers, during preparation of the compounds for academic purposes, and were in the main of an incidental nature.

During the period 1872–83 Linneman,¹ Caspary,² Fittig,³ Kahlbaum,⁴ and Weger⁵ recorded observations on acrylic acid, allyl acrylate, methacrylic acid, and methyl, ethyl, and propyl acrylates respectively. In most cases, difficulty was experienced in purifying the compounds in question by distillation on account of the ease with which they polymerized. The general effect of sunlight in accelerating polymerization was noted, as was the influence of heat. The polymers differed considerably in properties; thus methyl acrylate polymer was described as a transparent elastic mass, whilst polymethacrylic acid was a white porcelain-like mass, insoluble in organic solvents but swelling in water.

In 1900–2, Röhms, then a student working under von Pechmann,⁶ investigated the polymerization of methyl acrylate under the influence of metallic sodium, and showed that it underwent dimerization,



The dimer proved to be stable. Röhms's interest in the commercial

possibilities of the acrylate polymers is said to have been so aroused that he worked continually on the subject.⁷ In 1913 Röhm proposed that rubber substitutes be made by heating polymerized acrylic esters with sulphur,⁸ and shortly afterwards he foreshadowed their use for coating compositions or for impregnating wood and fabrics.⁹ The polymers were applied from organic solvents such as acetone and ethyl acetate.

The commercial exploitation of the acrylate polymers was hindered by lack of technically feasible methods of preparation, and it was not until about 1927 that real progress was possible. Improved methods for making acrylic esters were devised in Germany under Röhm's influence, and substantial advances made in the technique of polymerization, and in the form and qualities of the polymers. From this point, the acrylate resins have advanced rapidly, and an abundant literature on their preparation, polymerization, co-polymerization, properties, applications, and structure is now to be found.

The methacrylate polymers developed somewhat later; in this case the important advances were made in Great Britain.

The acrylate and methacrylate resins differ considerably in physical properties. Methyl acrylate polymer is soft and somewhat rubber-like, being extensible to the extent of 1,000 per cent.;⁷ on the other hand, methyl methacrylate polymer is quite hard, and is often referred to as 'organic glass'. On account of the wide divergence in physical properties, these polymers find quite different applications in industry.

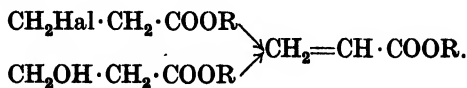
Within the short period which has elapsed since their introduction many novel applications have been uncovered. These resins are comparatively in their infancy, and the future prospects for their more widespread exploitation would appear to be particularly bright. The acrylate polymers are marketed under the names 'Plexigum' and 'Acronal'; methyl methacrylate polymer is known commercially as 'Diakon', 'Perspex', 'Lucite', and 'Plexiglas'.

Preparation of Acrylic Acid and Derivatives.

Many methods are now available for making acrylic acid and derivatives. Acrylic esters are formed by some of the reactions involved in making the acid by appropriate substitution.

Early academic methods were based on the direct oxidation of allyl alcohol and acrolein, but yields were low, and the conditions technically impracticable.¹⁰ Fairly recently, a technically feasible method is described for direct oxidation of acrolein in non-aqueous solution with air or oxygen, preferably under pressure, whereby good yields of acrylic acid are formed.¹¹

β -Hydroxypropionic derivatives and β -halogenopropionic derivatives readily lose the elements of water and hydrogen halide respectively, thus:



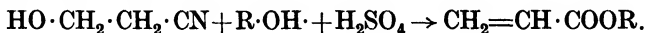
Dehydration of β -hydroxypropionic acid (hydracrylic acid) and esters is effected by the usual agencies. Beilstein¹² and Wislicenus¹³ used sulphuric acid; Van der Berg¹⁴ heated sodium β -hydroxypropionate to 140°, whereby it lost water, yielding sodium acrylate. Röhm and Haas used dehydrating agents such as sulphuric acid, phosphoric acid, and zinc chloride for the esters.¹⁵

Much of the early work on β -halogenopropionic derivatives was based on the bromo- and iodo-compounds. Alcoholic potash,¹⁶ sodium carbonate,¹⁷ and lead oxide¹² were all effective dehydrohalogenating agents under appropriate conditions (cf. 18).

Moureu¹⁹ preferred organic bases such as diethylaniline, and obtained practically theoretical yields of the methyl, ethyl, propyl, isopropyl, *n*-butyl, amyl, benzyl, methyl, and allyl esters of acrylic acid by this method. The ease with which hydrogen chloride is eliminated is illustrated by a process for treating β -chloropropionic esters with cold alcoholic alkali whereby removal is effected without hydrolysis of the ester group.²⁰ Substances containing inorganic acid radicals of low volatility such as sulphuric and phosphoric acids and zinc chloride, particularly when deposited on active carbon, are highly effective.²¹

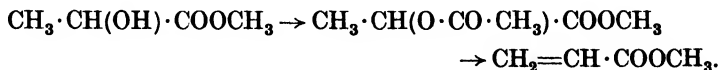
α - β -Dihalogenopropionic derivatives, and in particular the dibromo compounds, have been frequently used by academic workers as a source of acrylic acid and esters. The most favoured method appears to have been reduction with sulphuric acid and zinc,²² though many alternative methods have been described.^{2, 5, 17, 23, 24} Several processes have been patented for treatment of α - β -dichloropropionic esters with chlorine-removing agents such as finely divided zinc or aluminium activated with various agents.^{25, 26}

An attractive process for making acrylic esters consists in heating together ethylene cyanohydrin with sulphuric acid, the appropriate alcohol, and water.²⁷

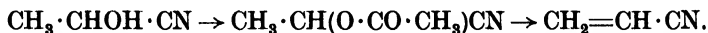


If the alcohol is omitted, and a sufficiency of water is present, then acrylic acid is formed.^{28, 29}

Although lactic esters do not appear to have been dehydrated directly into acrylic esters, nevertheless pyrolysis of the corresponding esters, e.g. methyl α -acetoxypropionate, affords good yields of methyl acrylate.^{30, 31, 32}



In a similar fashion acetaldehyde cyanohydrin gives rise to acrylonitrile.



It is claimed that acrylic acid is obtained by vapour-phase decarbo-

xylation of maleic acid or anhydride,³³ by the direct addition of ethylene and carbon dioxide,³⁴ both in the presence of silica gel. Pace³⁵ has stated that ethylene and phosgene unite to β -chloropropionyl chloride, which readily gives acrylyl chloride by vapour-phase dehydrohalogenation in the presence of a suitable catalyst,³⁶ but the former reaction has not been confirmed.³⁷

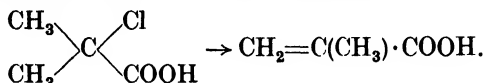
Acrylonitrile has been obtained in low yield by direct addition of hydrogen cyanide to acetylene.³⁸

Acrylic acid or chloroacrylic acid may be easily prepared from propionic acid ($\text{CH}_2=\text{C}(\text{CO}_2\text{H})$), obtainable from acetylene, by the action of carbon dioxide on sodium acetylide produced through the sodium addition product of naphthalene which with acetylene yields sodium acetylide.

Preparation of Methacrylic Acid and Derivatives.

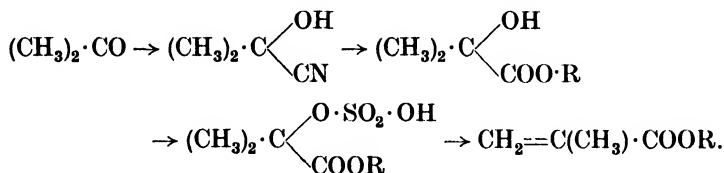
The preparation of these compounds has many points in common with the methods outlined in the preceding section.

Elimination of hydrogen halide and halogen from α -substituted isobutyric esters proceeds smoothly under appropriate conditions.^{39, 40}



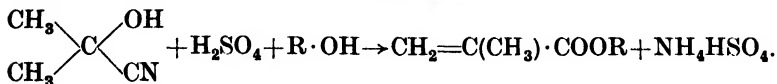
α -Hydroxyisobutyric esters obtained by hydrolysis and esterification from acetone cyanohydrin provide a convenient source of methacrylic esters. Early academic workers used phosphorus trichloride^{41, 42, 43} and phosphorus pentoxide⁴⁴ as dehydrants.

A technically feasible method utilizes chlorosulphonic acid; apparently in this case dehydration occurs through the intermediary of a sulphuric ester which undergoes decomposition.⁴⁵



As an alternative, α -hydroxyisobutyric esters are acetylated and the esters so formed submitted to pyrolysis.³⁰

A direct synthesis from acetone cyanohydrin consists in treating this compound with sulphuric acid or oleum followed by an alcohol.^{46, 47} Various esters have been made by this method; high yields are obtained by appropriate adjustment of conditions:⁴⁸

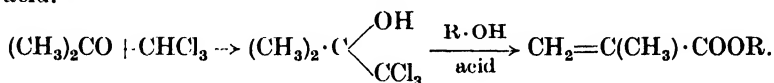


By using water in place of the alcohol, methacrylic acid is ob-

tained.⁴⁹ Direct action of sulphuric acid on acetone cyanohydrin in the absence of water and alcohols affords methacrylamide.⁵⁰

The technical development of methacrylic ester polymers has led to a systematic exploration of the less obvious derivatives. These include methacryloxy-carboxylic esters, prepared by interaction of an alkali methacrylate with halogenated esters;⁵¹ *n*-propyl methacrylate obtained by ester interchange;⁵² water-soluble addition salts of methacrylic acid and an amine alcohol in which the amine group is tertiary;⁵³ methacrylic acid ester mixtures in which the alcohol has been obtained by catalytic hydrogenation of carbon oxides;⁵⁴ diisopropyl carbinol methacrylate;⁵⁵ unsaturated alcohol esters of methacrylic acid;⁵⁶ alicyclic alcohols, tetrahydrofuryl methacrylates;⁵⁷ benzyl methacrylate;⁵⁸ resorcinol dimethacrylate;⁵⁹ and ethylene glycol monoethyl methacrylate.⁶⁰

An interesting method for making methacrylic derivatives consists in treating chloretone, obtained by treating acetone and chloroform with caustic potash,⁶¹ with water or an alcohol in presence of an acid.⁶²



Polymerization.

There are broadly four methods of importance for polymerization (cf. ⁶³); these are:

- (1) Direct homogeneous or mass method, in which the monomer is polymerized substantially in the absence of other substances.
- (2) Solution method, in which the monomer is dissolved in a solvent or solvent mixture which may or may not be a solvent for the polymer, and then polymerized.
- (3) Emulsion method, in which the monomer is dispersed in water, usually with the aid of emulsifying agents, and polymerized.
- (4) Granulation method, whereby the monomer is temporarily suspended in the form of discrete droplets in a non-solvent medium, and polymerized in this condition.

The general utility of the above methods is determined by the particular substance under consideration, and by the physical properties of the polymer.

In common with vinyl compounds, oxygen and oxygen-evolving substances function very actively as polymerization accelerators.⁶⁴ Thus, Staudinger⁶⁵ records that on heating methyl acrylate in an exhausted tube at 100° for 3 days there was no evidence of polymerization, yet on passing an air stream through the monomer, polymerization was complete in ½ hour. Benzoyl peroxide⁶⁴ and tetralin peroxide⁶⁶ are particularly valuable catalysts. Carbonyls of heavy metals are also claimed to be of value.⁶⁷ The properties of the polymers are affected by catalyst concentration, since molecular weight is reduced as temperature is increased.⁶³

Polymerization progresses more rapidly as temperature is raised; the operation is strongly exothermic, the heat of reaction in the case of methyl methacrylate being 80 cal. per gm.

It has been known from early academic workers⁴ that light accelerates polymerization, and the first polymerization patent in this field lays claim to polymerization of methyl acrylate under the influence of ultra-violet light.⁹

Nevertheless, Staudinger's experience with methyl acrylate is that polymerization under the action of light is erratic.⁶⁵ Some preparations were found to be stable for weeks, others only polymerized slowly, whereas in other cases polymerization proceeded rapidly with explosive violence.

As noted by Moureu in his classical research on antioxidants, phenolic substances and particularly hydroquinone act as strong polymerization inhibitors.⁶⁸ The use of small quantities of such stabilizers allows of the handling of the various monomers without the consequence of uncontrolled polymerization, and they have proved invaluable in this respect when preparing and purifying the monomers.

Polymerization can be effected in the presence of inhibitors, provided a sufficiency of polymerization catalyst is present.⁶⁹

When acrylic or methacrylic esters are polymerized by the direct homogeneous method, the mobile liquids increase progressively in viscosity, passing finally into elastic or hard glass-like masses. On the other hand, polyacrylic and polymethacrylic acids and the corresponding nitriles are insoluble in their respective monomers, and separate as polymerization proceeds.⁶⁵ This method is of particular importance for the production of sheets, rods, tubes, and shaped articles from methyl methacrylate. The main difficulties are the formation of bubbles due to overheating from heat development, and marks caused by the uneven contraction during the transition from the monomeric to the polymeric state. The methods include regulated heating,⁷⁰ casting in superimposed layers,⁷¹ retardation of polymerization at the edges of the mould by the addition of small amounts of inhibitors,⁷² polymerizing in rapidly rotating highly polished tubes,⁷³ by the use of layers of different viscosities,⁷⁴ or containing successively diminishing amounts of catalysts,⁷⁵ and the application of heat to the lower end of the mould in which the monomer is subjected to pressure.⁷⁶

The molecular weight of polymers produced by the solution method is lower than that obtained by other methods at comparable temperatures and catalyst concentrations. When the concentration of monomer is varied in a given solvent, the rate of polymerization and molecular weight of the polymer varies directly with monomer concentration.⁷⁷ Solution polymerization of acrylic esters may be carried out by passing oxygen through a refluxing solution in acetone.⁸⁷ Methyl methacrylate can be polymerized conveniently in aqueous ethanol of a composition adjusted to dissolve the monomer but not the polymer, which separates in the form of fine particles as poly-

merization progresses.⁷⁹ By appropriate adjustment of conditions polymers with improved heat resistance are obtained.⁸⁰ Whereas solution polymerization of the esters is usually conducted in organic solvents, the acids are frequently polymerized in water, in which the polymers remain dissolved or strongly swollen.⁸¹

Polymerization in aqueous emulsion is simple to carry out, and provides aqueous dispersions of polymers in a form in which they can frequently be used as such for various applications. The monomer is dispersed in water with aid of emulsifying agents such as soap, ammonium oleate, Turkey red oil, naphthalene sulphonic acid, and heated in the presence of suitable catalysts. The polymer is produced usually in the form of a fine latex-like dispersion.^{82, 84, 85} Alkali persulphates apparently combine the function of dispersing agent and catalyst and under these circumstances, no further additions are required. (Cf. also Chap. V, p. 200.)

The granular polymerization process is carried out in much the same manner as emulsion polymerization, except that emulsifying agents are replaced by protective colloids such as starch, gum tragacanth, and gelatine.⁸⁷ In the case of methyl methacrylate, the polymer is produced in the form of small spherical granules in a very suitable form for injection moulding. Other agents which can be used for this process include polyvinyl alcohol,⁸⁸ the gel-like resin obtained by polymerizing the reaction product of methyl methacrylate and ammonia,⁸⁹ calcium, barium, and magnesium persulphates,⁹⁰ and finely divided solid inorganic substances such as kieselguhr.⁹¹

In addition to the general principles already outlined for controlling and reducing the molecular weight of polymers, the addition of certain agents in small amount affords low molecular weight polymers. In particular, terpenes,⁹² and methallyl chloride⁹³ may be mentioned.

Properties and Applications of Polymers.

The properties of the acrylic polymers depend primarily upon the particular acrylic derivative concerned, and to a less extent upon the polymerization method involved.

In a polymeric homologous series there is a gradual decrease in hardness and thermal yield-point with increasing molecular weight of the alcohol. Thus methyl methacrylate polymer is amongst the hardest of the commercially available thermoplastic resins, and is practically unaffected by contact with boiling water. *n*-Butyl methacrylate polymer is soft and flexible at room temperatures. Branched-chain alcohols such as isobutyl methacrylate have a higher softening point compared with the corresponding straight-chain alcohols. With the straight-chain alcohol esters the tensile strength falls off as the molecular weight of the alcohol increases.⁹⁴ Some properties of the lower methacrylic ester polymers are summarized in the following table.⁹⁴

Properties of some methacrylic ester polymers

<i>Property</i>	<i>Methyl</i>	<i>Ethyl</i>	<i>n-Propyl</i>	<i>n-Butyl</i>	<i>Isobutyl</i>
Density at 25° C.	1.19	1.11	1.06	1.05	1.02
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	..

On the other hand, the acrylic ester polymers are comparatively low softening. Methyl acrylate polymer is extensible to the extent of 1,000 per cent. without plasticization. Films display a certain degree of plasticity and do not snap back sharply, but exhibit slow recovery.⁷ Polymers of high molecular weight have greater tensile strength, and recover more rapidly after elongation. As the homologous series is ascended, the polymers become progressively more plastic.

Polyethyl acrylate is softer and more elastic than the methyl ester, and not so tough. The polymer of *n*-butyl acrylate is so soft as to be sticky to the touch. Polymerized octyl and lauryl acrylates are semi-liquids. In common with the methacrylates, isomeric variations within the alcohol group have a marked influence on the properties of the polymer. The polymer of isobutyl acrylate is noticeably harder and tougher than that of the *n*-butyl ester, approximating in physical properties to *n*-propyl acrylate polymer. *Sec.*-butyl acrylate polymer is still harder, approaching the methyl ester in this respect. Although the *n*-butyl, isobutyl *sec.*-butyl acrylate polymers vary in their degree of softness, all of them are elastic and pliable. In the case of *tert.*-butyl acrylate, the polymer has lost practically all of its pliability, and is a hard tough solid. This seems to be the hardest of the aliphatic monohydric acrylate polymers. A carbon ring increases decidedly the hardness of the polymer. Cyclohexyl acrylate is quite hard and tough, whereas the *n*-hexyl ester is soft and tacky. Ethylene glycol diacrylate polymer is extremely hard and differs from the previous polymers in being insoluble in organic solvents.⁹⁵ (Cf. Chap. XV, p. 418.)

In contradistinction to the polymeric esters, polyacrylic and polymethacrylic acids and amides are insoluble in organic solvents, but are soluble in water or form water-soluble alkali salts. Polyacrylic nitrile is non-thermoplastic, and is insoluble in organic solvents.

The predominantly outstanding feature of the acrylic and meth-

acrylic ester polymers is their unique clarity and stability. They transmit a high percentage of light and are superior to glass in the transmission of ultra-violet light. They are absolutely fast to light, are unaffected by water, and are surprisingly resistant to inorganic agents. Thus at 50°, 60 per cent. sulphuric acid, 25 per cent. hydrochloric acid, 60 per cent. phosphoric acid, ammonia, and 20 per cent. sodium hydroxide are substantially without effect. These resins are very stable to heat. Methyl methacrylate polymer, for example, is not decomposed or discoloured at temperatures up to 200°; at 350° or above, it is depolymerized readily to monomer in good yield.⁹⁶ The thermo-conductivity is low, whilst dielectric strength and power factor are uniformly good; arc resistance is outstanding. The relatively low specific gravity is of considerable technical importance, and coupled with desirable features already enumerated has led to the widespread adoption of methyl methacrylate resins in the aircraft industry for windows, gun turrets, and cockpit enclosures. The optical properties make them suitable for use in spectacle lenses, camera lenses, magnifying glasses, protective goggles.⁷ The lenses can be produced either by casting the monomer¹⁰⁵, or by moulding the polymer.¹⁰⁶ A striking application is the mounting of biological or botanical specimens; the specimen is immersed in a syrup obtained by heating the monomer, and polymerization is completed by further heating.¹⁰⁷ Diffraction gratings can be produced by shaping the polymeride in a mould ruled with the desired pattern.¹⁰⁸ Coloured pictures and other ornamental effects are produced by engraving a workpiece consisting of two or more coloured layers of methyl methacrylate polymer.¹⁰⁹ This is also valuable for artificial dentures;¹¹⁰ for surgical splints,¹¹¹ where the transparency permits of perfect X-ray photographs and allows of periodic examination of wounds or skin without removal of the splints; for 'piping of light through material whereby light is conducted by internal reflection through a polished curved rod to emerge only where a frosted or curved surface is encountered'.⁷ The lower alkyl acrylates and higher alkyl methacrylates are valuable as interlayers for safety glass;¹¹² no sealing compound is required round the edges, which facilitates the use of odd-shaped sheets, whilst there is freedom from delamination. Safety glass made with these polymers is known as 'Plexite', 'Luglas', and 'Sigla'. Organic solutions and aqueous emulsions when applied to textiles provide permanent finishes. The harder resins give stiffness and sheerness to fabrics. The softer ones give body and fullness with a mellow handle.⁷ Laminated fabrics can be produced using an acrylate or methacrylate polymer as the bonding agent.¹¹³ The alkali salts of the polymerized acids are useful as dispersing, emulsifying, thickening, finishing, and sizing agents; the handle of rayon and cotton is improved by this treatment.¹¹⁴

In general, the polymers are soluble in aromatic hydrocarbons, esters, ketones, ethers, chlorinated hydrocarbons, and organic acids. As a rule, the solubility in alcohols, aliphatic hydrocarbons, terpenes, and drying and non-drying oils increases as the number of carbon

atoms in the esterified alcohol is increased. All of the polymers are insoluble in methanol, ethylene glycol, glycerol, and formamide. They are for the most part compatible with nitrocellulose, rosin, chlorinated rubber, vinyl chloride, and vinyl acetate interpolymers, and phenol aldehyde resins. The higher methacrylate polymers are more compatible with ester gum; the lower esters more compatible with polyvinyl acetate. They are not compatible with dammar, shellac, alkyd, hydrocarbon resins, cellulose acetate, and cellulose ethers. The methacrylate resins possess excellent film-forming properties because of their wide compatibility with solvents, plasticizers, and resinous materials, and because they are fast-drying, colourless, non-yellowing, adherent, tough, and durable.

By interpolymerization of selected acrylic derivatives with one another, or with other polymerizable compounds, special effects are frequently obtained. For example, methacrylic esters interpolymerized with a small amount of acrylic or methacrylic acids improves pigment compatibility;⁹⁷ interpolymers of 40–95 per cent. 2-ethyl hexyl methacrylate with methyl methacrylate are valuable for dressing, bonding, stiffening textile fabrics;⁹⁸ interpolymers of 30–98 per cent. methacrylic acid with 2–70 per cent. methyl methacrylate give water-soluble alkali salts, valuable for sizing viscose and rayon yarns;^{99, 100} methyl methacrylate interpolymerized with at least one other polymerizable ester¹⁰¹ gives valuable effects; 'organic' window glass is produced by interpolymerizing 30–90 per cent. acrylic nitrile with 70–100 per cent. methacrylic ester and 3–8 per cent. methacrylamide;¹⁰² and synthetic rubbers with exceptional abrasion resistance are obtained by interpolymerizing methyl methacrylate with butadiene.^{103, 104}

It will be clear from the foregoing examples that by appropriate selection of components, interpolymers having a very wide range of properties and applications can be devised.

REFERENCES

1. Linnemann, *Ann.*, 1872, 163, 360.
2. Caspary and Tollens, *Ann.*, 1873, 167, 241.
3. Fittig and Engelhorn, *Ann.*, 1880, 200, 65; *J.C.S.*, 1880, 38, 378.
4. Kahlbaum, *Ber.*, 1880, 13, 2348; 1885, 18, 2108.
5. Weger, *Ann.*, 1883, 221, 86; *J.C.S.*, 1884, 46, 8.
6. von Pechmann and Röhm, *Ber.*, 1901, 34, 427, 573.
7. Frederick, *Mod. Plastics*, 1938, Oct., 16.
8. Röhm, B.P. 613 (1913).
9. Röhm, G.P. 295,340.
10. Redtenbacher, *Ann.*, 1884, 47, 125.
11. Röhm and Haas, B.P. 373,326; B., 1932, 832.
12. Bellstein, *Ann.*, 1882, 122, 372.
13. Wislicenus, *Ann.*, 1873, 166, 2.
14. Van der Berg, *Rec. trav. chim.*, 1922, 41, 21.
15. Röhm and Haas, B.P. Appl. 37,815/30.
16. Schneider, *Ber.*, 1870, 3, 339.
17. Billmann, *J. pr. Chem.*, 1900, 61, 199.
18. Lossen, *Ann.*, 1905, 342, 128.
19. Moureu, *Compt. rend.*, 1921, 172, 1267.
20. Röhm and Haas, B.P. 316,547; B., 1930, 361.
21. I.G., B.P. 351,518; B., 1931, 1003.
22. Bucherer, *Ann.*, 1893, 273, 232.
23. Vorländer, *Ann.*, 1907, 294, 317.

24. Michael, *J. pr. Chem.*, 1891, **43**, 587.
25. Rohm and Haas, G.P. 555,933.
26. Rohm and Haas, G.P. 575,423.
27. Rohm and Haas, B.P. 313,877; B., 1930, 1143.
28. Imp. Chem. Ind., U.S.P. 2,026,894.
29. Triplex Safety Glass Co., B.P. 455,087; B., 1936, 194.
30. Imp. Chem. Ind., B.P. 424,885; B., 1935, 715.
31. R. Burns, D. T. Jones, and P. D. Ritchie, *J.C.S.*, 1935, 400.
32. P. D. Ritchie, *J.C.S.*, 1935, 1054.
33. I.G., B.P. 262,101.
34. Rohm and Haas, G.P. 553,179.
35. E. Pace, *Gazz. Chim. Ital.*, 1929, **59**, 578.
36. I.G., B.P. 333,079.
37. A. L. Klebanski and K. K. Tschevitschalova, *Ch. Abs.*, 1935, **29**, 6879; A., 1935, 845; *Chem. Zentr.*, 1938, **1**, 1335.
38. Consort. für Elektrochem. Ind., G.P. 559,734.
39. Lossen and Gerlach, *Ann.*, 1905, **342**, 159.
40. J. J. Sudborough, *J.C.S.*, 1909, **95**, 977.
41. Frankland, *Ann.*, 1865, **136**, 12.
42. Fittig, *Ann.*, 1877, **188**, 53.
43. Schryner, *J.C.S.*, 1897, **73**, 69.
44. Blaise, *Bull. Soc. Chim.*, 1905 (3), **33**, 761.
45. Imp. Chem. Ind., B.P. 409,733; B., 1934, 617.
46. Imp. Chem. Ind., B.P. 410,208; B., 1934, 710.
47. Imp. Chem. Ind., B.P. 410,457; B., 1935, 92.
48. Imp. Chem. Ind., B.P. 504,734; B., 1939, 696.
49. Imp. Chem. Ind., B.P. 405,699; B., 1934, 313.
50. Rohm and Haas, B.P. 467,492; B., 1937, 946.
51. DuPont de Nemours & Co., B.P. 496,892; B., 1939, 242.
52. Imp. Chem. Ind., B.P. 490,007; B., 1938, 1267.
53. DuPont de Nemours & Co., U.S.P. 2,138,762.
54. DuPont de Nemours & Co., U.S.P. 2,129,662.
55. DuPont de Nemours & Co., U.S.P. 2,129,663.
56. DuPont de Nemours & Co., U.S.P. 2,129,665.
57. DuPont de Nemours & Co., U.S.P. 2,129,666.
58. DuPont de Nemours & Co., U.S.P. 2,129,667.
59. DuPont de Nemours & Co., U.S.P. 2,129,685.
60. DuPont de Nemours & Co., U.S.P. 2,129,694.
61. Ostropjatow, *Beilstein. I. Syst.* 163, 421.
62. E. B. Thomas and H. F. Oxley, B.P. 505,103; B., 1939, 606.
63. H. R. Dittmar, *Chem. Trade J.*, 1938, **103**, 372.
64. Rohm and Haas, B.P. 304,681; B., 1930, 681.
65. Staudinger, *Helv. Chim. Acta*, 1929, **12**, 1107.
66. Rohm and Haas, F.P. 832,700.
67. I.G., B.P. 340,004; B., 1931, 333.
68. C. Moureu, *Compt. rend.*, 1919, **169**, 885.
69. Imp. Chem. Ind., B.P. 504,918; B., 1939, 860.
70. Rohm and Haas, U.S.P. 2,067,580; B., 1938, 1196.
71. DuPont de Nemours & Co., U.S.P. 2,063,315; B., 1938, 691
72. Imp. Chem. Ind., B.P. 474,242; B., 1938, 1075
73. Rohm and Haas, B.P. 475,552; B., 1938, 137.
74. DuPont de Nemours & Co., U.S.P. 2,136,424.
75. DuPont de Nemours & Co., U.S.P. 2,136,422.
76. DuPont de Nemours & Co., U.S.P. 2,136,423.
77. D. E. Strain, *Ind. Eng. Chem.*, 1938, **30**, 345.
78. Rohm and Haas, U.S.P. 2,073,619; B., 1939, 695.
79. DuPont de Nemours & Co., U.S.P. 2,135,443.
80. Rohm and Haas, B.P. Appl. 23,745/38.
81. H. Staudinger and H. W. Kohlschutter, *Ber.*, 1931, **64**, 2091.
82. I.G., B.P. 358,534; B., 1932, 172.
83. Rohm and Haas, B.P. 374,436; B., 1932, 878.
84. Triplex Safety Glass Co., B.P. 419,357; B., 1935, 93.
85. Triplex Safety Glass Co., B.P. 422,697; B., 1935, 263.
86. I.G., B.P. 494,772; B., 1939, 405.
87. Imp. Chem. Ind., B.P. 427,494; B., 1935, 599.
88. Imp. Chem. Ind., B.P. 444,257; B., 1936, 705.
89. DuPont de Nemours & Co., U.S.P. 2,133,257.
90. Imp. Chem. Ind., B.P. 505,012; B., 1939, 860.
91. Rohm and Haas, B.P. 455,242.
92. Rohm and Haas, B.P. 439,390; B., 1936, 207.
93. Rohm and Haas, B.P. Appl. 15,100/39.
94. D. E. Strain, R. G. Kinnelly, and H. R. Dittmar, *Ind. Eng. Chem.*, 1939, **31**, 382.
95. H. T. Neher, *Ind. Eng. Chem.*, 1936, **28**, 267.
96. DuPont de Nemours & Co., U.S.P. 2,030,901.
97. Imp. Chem. Ind., B.P. 478,323; B., 1938, 412.
98. Imp. Chem. Ind., B.P. 503,140; B., 1939, 714.
99. DuPont de Nemours & Co., B.P. Appl. 25,416/38.
100. DuPont de Nemours & Co., B.P. Appl. 11,636/39.
101. Imp. Chem. Ind., U.S.P. 2,117,321.
102. Rohm and Haas, B.P. Appl. 5,206/39.
103. Imp. Chem. Ind., B.P. 485,941; B., 1938, 1082.

104. Imp. Chem. Ind., B.P. 511,838; B., 1939, 1153.
105. Can. Ind. Ltd., Can.P. 377,393.
106. Lloyd, F.P. 831,404.
107. *Mod. Plastics*, 1938, 16, 60.
108. A. Hilger Ltd. and F. Twyman, B.P. 501,606; B., 1939, 632.
109. Röhm and Haas, B.P. 510,719.
110. Amal. Dental Co. Ltd., B.P. 498,877; B., 1939, 518.
111. *Mod. Plastics*, 1938 (Nov.), 34.
112. Röhm and Haas, G.P. 676,672.
113. Bleachers' Assoc. Ltd., B.P. 480,949; B., 1938, 1290.
114. I.G., G.P. 623,404.

CHAPTER VII

COUMARONE AND INDENE RESINS

By H. M. LANGTON

THE resins included under this description are formed by the direct polymerization of coumarone and indene* under the influence of catalyts of which sulphuric acid is by far the most important commercially. Aluminium chloride, ferric chloride, stannic chloride, and phosphoric acid also act as catalyts.¹ The use of sulphuric acid has the advantage over aluminium chloride that part of the raw material may be first resinified. The volatile material remaining from this part can be distilled and subsequently polymerized to give pale resins. The m.p. of AlCl_3 resins are up to 160° , whilst with H_2SO_4 resins the maximum is 65° . F. W. Sperr and M. Darrin² state that polymerization may also be effected by treating the naphthas under pressure in the presence of strips of metallic copper, silver, gold, or platinum.

A mixture of an acid sulphate of iron or other trivalent metal on an absorbent earth such as fuller's earth has been patented as a catalyst.³ The use of compounds of boron fluoride with hydroxy- or unsaturated organic acids has also been patented.⁴

Polymerization is also accelerated by oxidizing agents such as lead and other metallic resinates or linoleates.⁵ More violent oxidizing agents, such as potassium permanganate and bleaching-powder, react vigorously with coumarone, whilst the halogens unite with it to form the dihalides.

The raw material from which resins of this type are manufactured is solvent naphtha, which in addition to coumarone and indene contains other substances capable of resinification in the presence of sulphuric acid. As many of these resinous products are totally different from the resins produced from coumarone, and are by no means satisfactory from the point of view of industrial application, the careful selection and preparation of the solvent naphtha is a matter of great importance. Failure to appreciate this fact was responsible for many of the unsatisfactory products sold as coumarone resins and for the variation in properties, which has done much to discredit these resins in the eyes of the users in the past.

The principal resin-producing substances in coal-tar naphtha occur in the fraction boiling between 150° and 200° .

(1) Styrenes and cyclopentadiene.	B.p. below 160°
(2) Coumarone (b.p. 172°).	Fraction $168-75^\circ$
(3) Indene (b.p. 182°).	„ $176-82^\circ$
(4) Methylcoumarone.	„ $185-200^\circ$
(5) Methylindene.	„ $200-10^\circ$
(6) Dimethylcoumarone.	„ $215-25^\circ$

* For discussion on the polymerization of indene, cf. Chap. XV, p. 456.

Of these only coumarone and indene are suitable for the production of first-grade products. On polymerization with sulphuric acid cyclopentadiene gives black insoluble products and the styrenes thick viscous oils. The monomethyl homologues of indene and coumarone readily polymerize⁶ but cause the product to be too soft.⁷ The dimethyl coumarone does not polymerize.⁸

Even between coumarone and indene important differences exist in this respect, for whereas the polymerization of coumarone is only slightly exothermic that of indene is strongly so. Indene, as would be expected from its formula, is a much more reactive and unstable substance than coumarone. It is readily polymerized in an atmosphere of nitrogen at a temperature of 300–500°, whereas coumarone is practically unaffected.⁹ Indene can also be polymerized by heat, oxygen, or ultra-violet light (cf. styrene). Indene forms two para-indenes; one m.p. 165°, which is insoluble in ether-alcohol, and the other, m.p. 100°, which is soluble in ether-alcohol. The properties of indene polymers have been studied by G. S. Whitby and Morris Katz.¹⁰ The presence of indene in coal-tar naphtha was discovered by G. Kraemer and A. Spilker, who also first suggested the possibility of producing resins of industrial value by treatment of the solvent naphtha with sulphuric acid of over 80 per cent. strength.¹¹ Indene also yields resinous products¹² with acid of much lower concentration than does coumarone.¹³ It is claimed by M. Claasz¹⁴ that indene may be condensed with formaldehyde. Differences in the proportion of these two ingredients will therefore cause corresponding differences in the properties of the product, even when the process is otherwise carefully controlled. In practice, therefore, it is necessary to reduce the boiling range of the selected naphtha to within much sharper limits than 150–200°, in order to obtain first-grade and consistent products.

The progress of the reaction is also greatly influenced by the concentration of the polymerizable substances in the naphtha, the strength and proportion of the sulphuric acid, and by the time and temperature of reaction. The whole process, therefore, demands the highest degree of scientific control from beginning to end.

The process of manufacture falls into three stages:

- (1) The selection and purification of the naphtha.
- (2) Polymerization of the coumarone and indene.
- (3) Removal of the unchanged solvent naphtha.

(1) **Solvent naphtha.** The composition of solvent naphtha varies with the course and the method of distillation. In practice it is found that a naphtha distilling between 160° and 183° and containing about 30 per cent. of coumarone and indene, and free from acid or basic substances such as phenol and pyridine, is the most satisfactory, but the necessity for using so close a distillation range can be avoided by a preliminary treatment of the naphtha with a small quantity (0.1–0.5 per cent.) of sulphuric acid (66° Bé, s.g. 1.7). This results in the polymerization of the styrenes and cyclopenta-

diene which are removed by distillation. This process also removes tar bases which adversely affect the colour of the final resin. Wendriner¹⁶ used acid of 78 per cent. strength and a temperature of 100° for this preliminary polymerization.

A rather different line of work is suggested by the Rütgerswerke A.-G. patent,¹⁷ in which it is stated that by retaining the phenols in the naphtha an alcohol soluble resin, which can be used in the manufacture of spirit varnishes, is obtained.

(2) **Polymerization of the purified naphtha.** The patent literature indicates wide differences in practice both as regards the time and temperature of the reaction. Kraemer and Spilker (loc. cit.) and Wendriner (loc. cit.) used acid of 80 per cent. strength, the latter at a temperature of 40°. Stuart P. Miller,¹⁸ however, claimed that better results can be obtained by using much lower temperatures, 20° being the maximum, whilst even at -20° good results can be obtained.

J. Demant,¹⁹ on the other hand, proposes the use of weaker acid (about 60 per cent.), at a higher temperature.

The Barrett Company,²⁰ reduce the time of reaction to a minimum by passing the mixture of acid and naphtha between rapidly moving surfaces either in the form of vanes rotating between fixed baffles or of a cone moving in a fixed casing. The clearance is of the order of $\frac{1}{200}$ to $\frac{1}{10}$ in. and the peripheral velocity from 3,000 to 15,000 ft. per sec. The time of reaction is thus reduced to about 10 seconds. The chief difficulty encountered in the preparation of coumarone-indene resins from solvent naphtha by condensation with concentrated sulphuric acid is the rapid, uncontrolled rise of its temperature, occurring when reaction sets in, and leading to the formation of excessively polymerized material. G. K. Anderson²¹ uses glacial acetic acid as a diluent. Isopropyl ether may also be used as a diluent, but it is said that some danger is attached to the recovery of the isopropyl ether.

(3) **Recovery of the resin.** Whichever method has been used the spent acid has now to be removed and the residual naphtha containing the polymer distilled off.

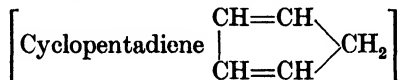
As regards the separation of the acid, trouble is sometimes encountered due to the formation of emulsions. It is claimed by the Barrett Company²⁰ that the adjustment of the percentage of resinifiable substance in the original naphtha is an important factor in dealing with this. The best results are obtained with a naphtha yielding about 30 per cent. of resin, and when the yield exceeds 45 per cent. the troubles due to the formation of emulsions become serious. Capthorne and Tannehill²³ control the degree of polymerization by diluting the heavy naphtha (150-200°) with lighter naphtha (130-50°) and arrest the reaction by passing in ammonia gas.²⁴ The use of saline solutions to break troublesome emulsions is described by H. Wade²⁵ and by S. P. Miller.²⁶

The acid layer having been removed, the naphtha is then distilled off. The last traces are removed either by maintaining the resinous

residue at a high temperature for some time or by placing it in a vacuum. The latter process sometimes results in the production of a cloudy-looking product due to the presence of air bubbles. This, of course, is quite immaterial from the user's point of view and should be distinguished from cloudiness caused by the presence of salts, such as sodium sulphate, due to the insufficient washing of the naphtha solution prior to distillation. The yield of resin varies naturally with the composition of the raw material, but is generally of the order of 0.2 per cent.²⁷

According to a patent by the Neville Company,²⁷ in the bulk production of coumarone resin an activated bath is prepared by dispersing a catalyst, e.g. sulphuric acid in distilled or refined naphtha, in a liquid diluent, which is inert to the polymerization reaction and is a solvent for the resulting resin, but in which the catalyst is insoluble; placing the activated bath in an apparatus arranged for cooling it, and gradually adding, e.g., crude solvent naphtha containing substances polymerizable to coumarone resin at a suitably slow rate.

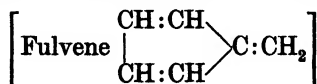
The main difficulty with coumarone resins in the past has been to remove impurities that spoil colour, odour, and other properties. Recently W. H. Carmody, W. E. Sheehan, and H. E. Kelly²⁸ have described the workings of a full-scale plant, in which the charging stock contains 60-5 per cent. of dicyclopentadiene, 15-20 per cent.



of indene, and 5-10 per cent. of coumarone. Heat polymerization is the method employed and the resultant resins are mainly polymers of dicyclopentadiene. These resins, which have very little colour, are remarkably resistant to acids, alkalis, and brine solutions.

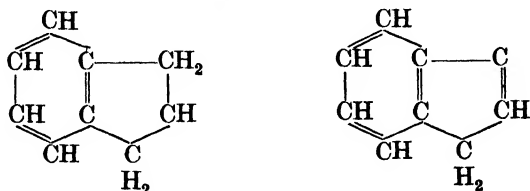
The same authors²⁹ attribute the yellowing of indene-coumarone resins to the development of a highly unsaturated molecular structure belonging to the fulvenes. Hydrogenation prevents the formation of these highly coloured bodies in the resinous mass, by preventing a series of reactions beginning with the entry of oxygen and its subsequent expulsion as water. Many factors affect the reaction, but a water-white resin can now be produced on a small scale by operating at 1,000 lb. per sq. in. pressure, 200°, 70 per cent. resin concentration, and a cycle of 20 hours.

W. E. Sheehan, H. E. Kelly, and W. H. Carmody,³⁰ discussing the oily dimerides derived from indene and coumarone, postulate the persistence of a cyclopentadiene ring during polymerization which they claim is shown by the formation of highly complex coloured fulvenes when indene, &c., aided by alkali metal alcoholates, react with ketones.



Their suggested configuration for indene polymerides is in contrast

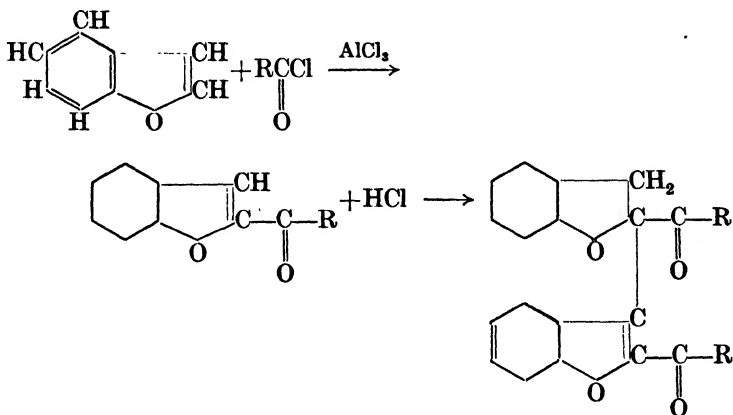
to the suggestion of Staudinger and Whitby and Katz, as it shows the double bond common to both rings:



It is further claimed that these oily dimerides, because of their high solvent strength and low volatility and chemical inertness, are particularly useful in chlorinated rubber coatings, lacquers, adhesives, inks, and water-proofing compositions.

Fatty-acyl-modified resins of dicyclopentadiene, coumarone, and indene types have been described by A. W. Ralston, R. J. V. Wal, S. T. Bauer, and E. W. Segebrecht,³¹ who have introduced high acyl groups into the polymers in order to give a high degree of flexibility, combined with resistance to chemical attack and conferring a reasonable hardness.

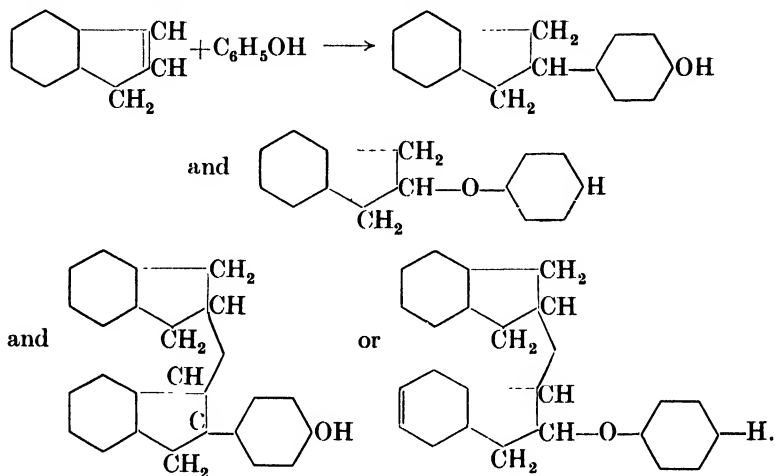
A Friedel-Craft's reaction is carried out on (a) crude solvent naphtha containing as a major constituent coumarone, indene, or cyclo-pentadiene respectively, together with lesser amounts of the other two; or (b) a commercial coumarone resin formed by polymerization of commercial coumarone. The acid chloride, stearoyl, oleyl, linolenoyl, is added, tetrachlorethane being the solvent for the resin-forming bodies. To this solution the anhydrous aluminium chloride is slowly added at 25°. The time of addition is 2 hours, and after this period, the reaction temperature is raised to 50° for 2 hours.



J. Rivkin and W. E. Sheehan³² have described the production and properties of phenol-modified indene-coumarone resins. The

reaction is based on the use of crude solvent naphthas and ordinary commercial phenols, a new activated clay being the catalyst in preference to acids or metallic chlorides. These phenol-modified resins are soluble in alcohol, and are compatible with many natural plasticizing resins, cellulosic products, pliolite, &c.

Increasing the proportion of phenols improved the alcohol solubility of the resulting reaction products, and their content of viscous oily products, and resulted in a lowering of the m.p. as well as of the molecular weight of the hard resinous product.



The use of phenol as a modifier in this way has been described in patent literature by L. Rosenthal and W. Kropp,³³ and by L. Rosenthal.³⁴ The latter incorporates a bromo-fluor-fatty acid as the catalyst. All these resins are said to be colourless.

Grades of Coumarone Resin.

According to the quality of the raw materials and the method of manufacture a wide range of products can be obtained and as many as forty different commercial grades have been described, ranging from almost black to very pale yellow, and from plastic masses to hard brittle solids melting at over 120° . The softer grades are used in the rubber industry, whilst the palest and hardest are used in varnish manufacture. T. Hedley Barry³⁵ describes a typical series of coumarone resins.

(1) *American varnish grade*. Used for spirit varnishes and cellulose lacquers. M.p. $120-130^\circ$. Pale yellow colour, completely soluble in benzene giving a hard brittle film. Free from acidity. [J. Bojanowski, B. Gizinski, and T. Rabek state that practically colourless resins are obtained by conducting the polymerization in the presence of 15:4:1, H_2SO_4 -Ac OH- H_2O .]³⁵

(2) *American*. Used for printing-ink varnishes. M.p. $100-110^\circ$.

Dark-brown-black in colour. Insoluble in benzene (1.1 per cent.). Gives hard brittle film. Free from acidity.

(3) *British dark grade*. M.p. 55–65°. Almost black in colour. Insoluble in benzene (2.16 per cent.). Gives a soft sticky film. Sulphuric acid present.

(4) *British soft grade*. M.p. 30–35°. Light brown in colour. Completely soluble in benzene giving soft film. It contains traces of acid.

(5) *A German resin*. M.p. 40–45°. Pale yellow in colour. Completely soluble in benzene. Free from acid.

The classification of coumarone resins has been carefully studied in Germany by the Cumaronharz-Verband G.m.b.H., Bochum, and a detailed account of the methods used has been given by J. Scheiber and K. Sändig.³⁶

PHYSICAL AND CHEMICAL PROPERTIES OF COUMARONE RESINS

Physical Properties and Tests.

(1) *Behaviour on heating*. On heating the harder coumarone resins they soften and melt, the change usually taking place within about 10°. Coumarone resins do not possess any appreciable thermoplastic properties, and on heating begin to decompose about 275°, this change being complete at high temperatures.

(2) *Solubility*. Coumarone resins are soluble in a wide range of substances, practically all the usual oils, thinners, and solvents used in the manufacture of varnishes and cellulose lacquers, with the exception of alcohol. Special attention, however, must be paid to the case of petroleum distillates.

(a) *Petroleum hydrocarbons*. The resins of lower melting-points are readily soluble in the usual petroleum distillates or white spirits, but those of higher melting-points, which are mainly used in varnish and lacquer manufacture, do not yield stable solutions with petroleum distillates deficient in cyclic or aromatic hydrocarbons. Petroleum thinners derived from asphaltic oils are therefore to be preferred to those from paraffin bases. It is important, in any case, to test the petroleum thinners to be used, and it is desirable to include some aromatic hydrocarbons—such as benzene, xylene, or solvent naphtha—in the formula. Turpentine is also satisfactory in this respect. From 10 to 15 per cent. (calculated on the total thinners) of such solvent is sufficient to ensure stability in the majority of cases, though with very high melting-point resins as much as 20 per cent. may be advisable. Concentrated solutions of the resin are more stable than dilute ones, showing that this is a case of mutual solubility. Stability of solution is still further increased by the presence of rosin or vegetable oils such as linseed or China wood-oil.

(b) *Solubility in benzene*. Pure coumarone resins are completely soluble in aromatic hydrocarbons. It should be noted that metallic impurities may be present in the form of soluble compounds, such as resinates or other organic salts, and therefore the part insoluble in benzene does not necessarily include all the mineral matter. An

examination of the film produced on glass by solution of the resin in an equal weight of benzene affords much information as to the properties of the resin from the varnish point of view. A good varnish grade will give a hard brittle film in less than 2 hours, whilst the soft grades yield sticky films which do not dry hard even after several days.

(c) *Vegetable oils*. Coumarone resins are miscible in all proportions with linseed and other oils, but not with castor oil. They are soluble in bodied oils, but less so in blown oil. With heavy blown oils it is desirable to include refined or polymerized oils in the formula.

(d) *Waxes*. Coumarone resins are miscible with natural or synthetic waxes in all proportions, with the exception of paraffin wax, in which case a minimum of 70 per cent. of resin is necessary to produce a permanently homogeneous mixture.

(e) *Solubility tests*. J. Marcusson³⁷ devised a test based on the fact that the lower polymers of indene and coumarone are soluble in ether-alcohol mixture, whilst the dark-coloured substances are insoluble in acetone.

Three grammes of the resin are dissolved in 15 c.c. ether and the solution cooled to 0°; 45 c.c. of 96 per cent. alcohol are added slowly. After standing 30 minutes the precipitate is filtered off and washed with 15 c.c. of ice-cold 96 per cent. alcohol. The filtrate is evaporated and the soluble resin weighed. The insoluble residue on the filter-paper is then extracted with acetone and the residue, which consists of asphaltic bases, weighed. The percentage of organic matter insoluble in acetone and in the ether-alcohol mixture varied from nothing in the pale resin to 12.5 per cent. in the black, whilst the soluble in ether-alcohol mixture increased with the depth of colour, a pale very hard resin containing 47 per cent. whilst a very hard black resin contained 64 per cent. A thick dark viscous resin gave 84 per cent. soluble in ether-alcohol and 2 per cent. organic matter insoluble in acetone and in ether-alcohol.

Chemical Properties and Tests.

(1) *Acid and saponification value*. Coumarone resins are completely unsaponifiable and neutral and should therefore give no appreciable values when tested by the usual methods. In practice the acid value is of the order of 0.3 and the saponification value 5.0.

(2) *Iodine value*. Iodine values up to about 25 are encountered, due mainly to the presence of polymers of indene which, in contradistinction to coumarone polymers, are capable of combination with iodine and also with oxygen.

(3) *Reaction with bromine*. According to Carleton Ellis⁴² coumarone resins can be distinguished from natural resins by their reaction with bromine, the test being carried out as follows:

One cubic centimetre of a 10 per cent. solution of the resin in chloroform is diluted with 6 c.c. of chloroform and 1 c.c. of glacial acetic acid added. The solution is shaken and 1 c.c. of a 10 per cent.

solution of bromine in chloroform added. The bottle is stoppered, shaken, and then allowed to stand. A permanent red colour develops on standing, whereas pontianak copal gives a yellow colour. As little as 10 per cent. coumarone resin causes a permanent orange-red colour.

(4) *Behaviour with sulphuric acid.* Fifty cubic centimetres of a 10 per cent. solution of the resin in carbon tetrachloride is shaken with 3 c.c. of concentrated sulphuric acid. The solution is then washed with alkali and finally with water and the resin recovered by evaporation. With good resins at least 9 per cent. of the resin should be recovered practically unchanged. This test is important as indicating the extent to which the resin has been freed from incompletely polymerized and basic substances.

(5) *Dry distillation.* Coumarone resin is decomposed on heating to 300–400°, coumarone, indene, and hydrindene being the main products. By redistilling the distillate these substances can be identified in the fraction of the distillate boiling between 160° and 180° and the presence of the resin thus established. Coumarone and indene are best identified by formation of their picrates which melt at 102° and 98°, respectively.

(6) *Heating with soda lime.* Only negligible quantities of phenol should be obtained from properly prepared coumarone resins. The reaction is therefore useful in detecting the presence of phenol formaldehyde resins. According to Marcusson (*loc. cit.*) the test is best made by heating 1 gm. of the resin with 5 gm. of soda lime in an oil-bath at 260° for 2 hours and then extracting with warm water. The presence of phenols is then indicated by a precipitate appearing on acidifying with hydrochloric acid or by the formation of a red azo-dye on addition of diazobenzene to the alkaline solution. Pure coumarone resin should not give more than a faint red coloration with diazobenzene or a very faint cloud with hydrochloric acid. Phenols can also be detected by Liebermann's reaction. A small piece of sodium nitrite is dissolved in 5 c.c. of concentrated sulphuric acid. On adding about $\frac{1}{2}$ gm. of the resin a brown solution is obtained which, if phenols be present, turns blue on warming. The mixture is poured into water and a red colour, which turns blue on adding caustic soda, denotes the presence of phenol.

(7) *Behaviour with aqueous alkali.* Coumarone resins are unaffected by 5 per cent. solutions of sodium carbonate, but with 10 per cent. caustic alkali a slight reaction occurs on warming. Generally, coumarone resins are chemically inert and very stable.

Methods of Grading.

Coumarone resins are graded mainly by colour and melting-point. The methods by which these properties are determined vary, and consequently direct comparison between the figures given by different manufacturers is not always possible.

(1) *Melting-point.* (a) *Cube in air method.* A $\frac{1}{2}$ in. cube of the resin is cast on the end of a copper wire and suspended in an air-bath beside the bulb of a thermometer. The temperature is raised at a

rate of 3° per minute, and the temperatures at which the resin commences to soften and finally drops off the rod are noted.

(b) In place of an air-bath a mercury bath is used and the cube immersed in it. The temperature at which the resin rises to the surface is noted as the melting-point. Provided this test is carried out under standard conditions the relation between the true melting-point and that found is practically constant. Corrected melting-point = mercury test $\times 1.25 + 2$.

(c) *Kraemer-Sarnow method.* About 25 gm. of the resin is melted and poured into a glass tube 6 to 7 mm. in diameter to a depth of 5 mm. On top of the solidified resin is poured 5 gm. of mercury. The bottom of the tube is then removed. The tube is suspended in a water-bath and heated at a rate of 1° per minute. The temperature at which the mercury falls through the resin is taken as the melting-point.

The results from the ring-and-ball method have been correlated by the Barrett Company (Circ. p. 39) with those from the cube-in-air method.

The ring-and-ball results can be converted to Kraemer-Sarnow figures by the formula:

$$K = 0.95R - 10;$$

where

$$K = \text{Kraemer-Sarnow M.P.},$$

$$R = \text{ring-and-ball M.P.}$$

(d) Various forms of penetrometer tests have been suggested. The time taken by a standard nail or needle to penetrate a given depth into the resin at a known temperature is taken as a measure of the hardness. J. Marcusson³⁷ describes the test using a '5 in. round' wire nail, weighing 23 to 25 gm. and 130 mm. long. The resin is filled into a vessel 8 to 10 cm. in diameter to a depth of 15 to 20 cm. and the test made at 20°. The time (generally not more than 5 sec.) taken for the nail to sink to the head is measured. This test, however, can only be used at 20° for the softer resins with softening-points below 30°. With resins harder than this, the temperature must be raised to ensure sufficiently rapid sinking of the nail.

(2) *Colour.* The colour of the resin is measured by comparison with a solution of known chemical composition and concentration. The German practice is to compare the colour of a solution of the resin in benzene with that of a solution of 15 gm. of potassium dichromate per litre of 50 per cent. sulphuric acid. The resins are then graded as follows:

- (a) 10 per cent. solution of coumarone in benzene not darker than the standard dichromate solution.
- (b) 2½ per cent. solution not darker than standard dichromate solution.
- (c) Artificial light penetrates 10 per cent. solution of the resin.
- (d) Artificial light (50 candle-power) penetrates a 15 mm. layer of 5 per cent. solution of the resin.
- (e) Artificial light does not penetrate 5 per cent. solution of the resin.

A more detailed series of colour standards has been worked out by the Barrett Company of New York.³⁸

A solution of 2 gm. of resin in 25 c.c. benzole is matched against the following series of standard solutions:

A. *Stock Acid Solution.* 25 c.c. 33.6 per cent. HCl in 975 c.c. water.

B. *Stock Iron Solution.* 100 gm. FeCl₃·6H₂O in 60 c.c. stock acid solution.

C. *Stock Cobalt Solution.* 50 gm. CoCl₂·6H₂O in 50 c.c. stock acid.

Two grammes of the resin are dissolved in 25 c.c. pure benzene, and compared with solutions made by mixing the above standard solutions.

Ten standard colours are obtained as follows:

	A (c.c.)	B (c.c.)	C (c.c.)	Distilled water (c.c.)
1	250	2.0	1.5	..
1½	250	2.8	1.0	..
2	250	4.0	2.5	..
2½	250	5.6	3.2	..
3	250	8.0	4.0	..
3½	..	13.2	4.0	250
4	..	16.0	4.0	250
5	..	20.0	5.5	200
6	..	40.0	10.0	200
7	..	80.0	15.0	200
8	..	130.0	10.0	100
9	..	250.0	20.0	55
10	..	250.0	20.0	..

Using the cube in mercury for the determination of the melting-point and the above standard of colour measurement the Barrett Company arrange coumarone resins in the following series:

Type	Grade	Colour (not darker than)	Melting-range		Ash (less than)
			°C.	°F.	Per cent.
High Melting	W	½, 1, 1½	150-60	300-20	0.1
Varnish	V	½, 1, 2, 3½	127-42	260-70	0.1
Rubber:					
Special Soft	R 30	8	20-40	68-104	1.0
Rubber Soft	RS	8	40-58	104-36	1.0
Rubber Hard	RH	4	77-95	170-203	1.0
Medium:					
Medium Soft	MS	8	58-77	136-70	1.0
Medium Hard	MH	4	105-27	220-60	0.5
Plastic					
	P 10	1-2½	5-15	40-59	0.1
	P 25	..	20-30	68-85	0.1
'X'					
	AX	10	20-30	68-85	1.0
	BX	10	35-45	95-113	1.0
	CX	10	45-55	113-31	1.0
	DX	20	75-85	167-85	1.0
	EX	20	100-15	212-40	1.0
	FX	20	125-30	255-65	1.0

Coumarone resins are used in a variety of industries, particularly where their chemical inertness is of value, but their consumption in Great Britain is small. The principal uses are in the manufacture of varnishes and printing-ink mediums and in the rubber industry. Coumarone resins are also used in the preparation of various coatings which are required to be resistant to water and chemical action. Although they have no thermal-hardening properties, these resins are useful ingredients of some types of moulding preparations, an important characteristic being that their insulating properties are less affected by changes in humidity than is the case with many other resins. This characteristic also makes them particularly suitable for insulating varnishes. The general uses of coumarone in industry are discussed by T. Hedley Barry,³⁹ J. Greenfield,⁴⁰ R. Green,⁴¹ by Carmody, Sheehan, and Kelly,²⁷ by H. Barron and others.⁴² R. I. Emery⁴⁴ and A. Joachim⁴⁵ deal with the use of coumarone resins in varnishes and cellulose lacquers.

Oil Varnishes.

In the manufacture of oil varnishes particular attention has to be paid to the fact that the resin, being practically inert, does not react with the other constituents of the varnish. Careful adjustment of the proportion of thinners, &c., and very thorough cooking of the gum-oil mixture to ensure stability of the final product is necessary. The addition of a proportion of rosin, particularly in long-oil varnishes containing China wood-oil, is recommended by some writers with the object of increasing the stability of the varnish. When China wood-oil is used it has also to be remembered that coumarone resins do not regard gelation in the same way as does rosin. This chemical inertness also affects the choice of driers, and it is advisable that the metallic content should be kept as low as possible.

Generally speaking, cobalt is the most satisfactory drier. When lead is used it is preferable to use the resinate.

When making varnishes in which a pale colour is required it is desirable to avoid over-heating as darkening becomes marked at temperatures over 550° F., though the better grades of coumarone are not unduly sensitive in this respect. Temperatures up to 570° F. can usually be employed without excessive darkening.

Coumarone resins are not oil reactive, though some writers⁴⁶ state that they have a retarding action on the gelation of China wood-oil; this effect, if it exists at all, is very slight, and in practice the manipulation of coumarone China wood-oil mixtures at high temperatures (above 280° C.) requires very great care. It will be noted that in the formula for short-oil varnish part of the coumarone resin is withheld till the latest possible minute in order to check gelation by cooling the mixture. At the same time thorough cooking is essential as, apart from the danger of webbing in the resulting varnish, the coumarone tends to precipitate unless thoroughly incorporated with the oils.

Coumarone varnishes of all types can be made and the following typical formulae may be quoted as examples of the usual procedure:

(1) *Spar Varnish (Long Oil)*.

100 lb.	China wood-oil
14 lb.	Rosin.

Heat to 530° F. until a drop strings on cooling, then add

50 lb.	Linseed oil
100 lb.	Coumarone resin varnish grade.

Raise the temperature to 550-5° F. for about $\frac{1}{2}$ hour, then add

2 lb.	Cobalt resinate (1 per cent. Co).
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Cool and thin with

150 lb.	White spirit
50 lb.	Solvent naphtha.

(2) *Short Oil Varnish*.

100 lb.	China wood-oil
80 lb.	Coumarone resin.

Heat to 530° F. until a drop sets hard on cooling, then add

26 lb.	Coumarone resin
$6\frac{1}{2}$ lb.	Cobalt linoleate (1 per cent. Co).

Heat for about $\frac{1}{4}$ hour at 550° F. Cool and thin with

300 lb.	Turpentine.
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By the use of a mixture of driers and rather higher temperatures quick-drying varnishes (four-hour) can be made. The use of rosin or lime-hardened rosin is desirable, though not essential, in order to facilitate control of the China wood-oil at high temperatures.

(3) *Four-Hour Varnish*.

100 lb.	China wood-oil.
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Heat to 400° F., then add

6 lb.	Lime-hardened rosin
40 lb.	Coumarone resin.

Heat rapidly to 560° F. and maintain until the varnish strings to about 12-15 in., then add

40 lb.	Coumarone resin
3 lb.	Lead resinate (20 per cent. Pb).

Maintain at 490-500° F. until desired body is reached, then add

150 lb.	White spirit,
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followed by

1 lb.	Manganese drier (1 per cent. Mn)
3 lb.	Cobalt drier (1 per cent. Co).

The China wood-oil can be partly replaced by linseed oil, but the drying time is reduced.

A rather different procedure is described by W. W. King, F. W. Bayard, and F. H. Rhodes,⁴⁷ who describe the preparation and

properties of a wide range of varnishes. They prefer to heat the mixture of linseed and China wood-oil (about 15 parts linseed and 100 parts China wood-oil) and resin to about 575° F. until the desired body is attained, and then cool rapidly to about 270° F., when the thinners and driers are added. Solvent naphtha is used as a thinner. A lead-cobalt drier dissolved in linseed oil and thinned with naphtha is used.

R. I. Emery⁴⁸ states that the addition of 3 per cent. phenol to long-oil coumarone varnishes improves the quality. By the use of 1 per cent. litharge and 0.06 per cent. of cobalt acetate in 16-gallon varnishes films drying in 4 hours can be obtained. The production of four-hour varnishes is also described by R. S. Green.⁴⁹

Coumarone varnishes properly made are quite satisfactory and compare favourably with those made from natural or other synthetic resins. Most of the troubles which arise are due to incomplete amalgamation of the resin with the oil, or to inadequate control of the China wood-oil during the cooling process. Blooming and checking are the most frequent troubles. The danger of the former is much reduced by the addition of rosin, and both are avoided by careful attention to the points already stressed.

Enamel Mediums.

The inertness of coumarone resin and the consequent low acidity of the resulting varnish renders it very suitable for use in enamel mediums, particularly when basic pigments are to be used. In common with most synthetic resins a slight though distinct yellowing occurs, which limits the scope of these media in that they cannot be used where pure whiteness is required. The yellowing reaches a maximum in about 48 hours, and would appear to be an oxidation effect.

Spirit Varnishes and Lacquers.

Solutions of coumarone resins in various solvents are used for a variety of purposes. Kraemer and Spilker⁵⁰ suggested the use of a solution of the resin in benzene and similar solvents as a protective coating. The use of a number of other solvents has been described.⁵¹ Carleton Ellis⁵² describes the use of such solutions for the treatment of concrete in order to render it damp-proof, and Fehringer⁵³ claims the use of coumarone spirit varnishes in the manufacture of bronzing preparations. In both cases the value of coumarone depends upon its chemical inertness.

Similar preparations are also used for water-proofing fabrics.⁵⁴ More recently solutions of hard-grade coumarone resin in solvent naphtha have been used for road-marking paints, which are required to be very fast drying, resistant to water, and strongly adhesive.

Used alone, coumarone yields rather brittle films, and the addition of a plasticizer is necessary. Castor oil is generally used. Coumarone has the advantage that it yields less viscous solutions than does damar at corresponding concentrations, and it is therefore possible

to obtain a higher concentration of non-volatiles in the film and a corresponding increase in the opacity of the paint.

Coumarone solutions have also been used for impregnating moulded articles made with asbestos and similar substances in order to increase their water-resisting and insulating qualities.⁵⁵

Cellulose Lacquers.

The paler and harder resins are suitable for use in cellulose lacquers, though the presence of another resin, preferably ester gum, is apparently essential. Coumarone increases the hardness and gloss of the film and improves the adhesion. A. Rogers and C. Banta⁵⁶ found that a ratio of 4 parts of coumarone to 7 parts of ester gum gave the most satisfactory results. Dibutyl phthalate was found to be the most satisfactory plasticizer. Castor oil can also be used. Coumarone resins do not retain the solvent, and therefore are particularly suitable for use in quick-drying rubbing lacquers. The coumarone can be dissolved with the other resins, natural and synthetic, and the oils. A typical formula is given by Rogers and Banta.⁵⁶

½ sec. Nitro-cotton (30 per cent. alcohol)	.	.	8
Butanol	10
Toluol	31
Ethyl acetate	10
Butyl acetate	25
Dibutyl phthalate	5
Ester gum	7
Coumarone resin	4

In order to improve the flowing qualities linseed oil may be added, from 3 to 4 per cent. being sufficient.

A. Jones⁵⁷ gives numerous examples of cellulose lacquer formulae containing coumarone resins.

Insulating Varnishes.

The chief merit of coumarone lies in the fact that its electrical resistance does not vary so greatly with changes in humidity as in the case of many other substances.

Surface Resistivity

	<i>Humidity 30%</i>	<i>Humidity 90%</i>	<i>Dielectric constant</i>
Coumarone	1 × 10 ¹⁵	1.5 × 10 ¹⁴	3.50
Shellac	3 × 10 ¹⁴	8 × 10 ⁹	3.10
Mica	2 × 10 ¹⁴	8 × 10 ⁹	..
Glyptal Resin	2 × 10 ¹⁵	3 × 10 ¹²	..
Rosin	1 × 10 ¹⁵	2 × 10 ¹⁴	2.50
Paraffin Wax	100 × 10 ¹⁵	100 × 10 ¹⁵	..

Other important electrical properties include high breakdown strength, low power factor, and high dielectric strength.

Moulded Articles.

Although possessing no thermoplastic properties coumarone resins are used to some extent in moulding where their water-proofing and electrical insulating properties are of value. Baekeland⁵⁸ proposed the addition of coumarone resin to phenol-formaldehyde condensation products, and McCoy⁵⁹ described the use of coumarone in conjunction with vegetable oils as a binder in moulded articles containing asbestos and similar materials. In conjunction with shellac coumarone resins have been used in the manufacture of binders for grinding wheels.⁶⁰

Coumarone and indene resins are inherently brittle and plasticizers have not been successful in overcoming this disadvantage for use in moulding plastics.

In cold-moulded articles coumarone resins are employed with phenol-formaldehyde resin in moulding electrical parts. Though primarily of use as softeners, they confer glossiness on the finish of moulded articles.

Rubber.

Coumarone is used to a considerable extent in rubber mixings. The principal grades used are:

Hard	m.p. 77-95°
Medium	m.p. 40 58°
Soft	m.p. 35-40°

The soft grades are used mainly in the manufacture of adhesive tapes and in friction compositions, whilst the harder varieties are used in the manufacture of various articles such as shoe heels, rubber water-bottles, tyre stocks, rubber flooring, hose, &c.

Coumarone has no effect upon the ageing properties of rubber or upon the vulcanizing process, but has important influence upon the milling properties. Above its melting-point coumarone acts as a solvent for rubber and for sulphur, and thus exerts a softening influence, which considerably reduces the time and labour involved in milling. For hard goods, up to 7 per cent. coumarone is required, whilst for soft goods as little as 2 per cent. is sufficient. Used in these quantities colour is not of material importance and the medium dark grades can therefore be used.

Coumarone resins are very useful ingredients in rubber solutions and as emulsions they are now finding application in the field of rubber latex. They are also used in compounding Neoprene, Thiokol and in the Bunas; moreover, they are displacing rosin in rubber because the mixture ages better.

Minor Uses.

In addition to the above, which constitute the principal outlets for coumarone resin, it is used in smaller quantities for various other materials, such as chewing-gum, where it can be used partially to

replace chicle. Specially purified grades, however, are essential, and not more than about 10 per cent. can be incorporated.

In moulding materials coumarone is limited by its brittleness, but is used to some extent in conjunction with such materials as asphaltum in both hot and cold mouldings.

Lender and Koch⁶¹ first suggested its use in the manufacture of linoleum in conjunction with China wood-oil. Further developments in this direction were described by G. W. Priest.⁶²

The use of coumarone in sizes for paper, felt, and cloth has also been described.⁶³

In printing-inks coumarone can be used in order to body the oil, and it is claimed that the gloss and stability of the ink is improved.

Coumarone resins readily mix with binder materials and with tars, pitches, &c. They are compatible with copal, rosin, ester gums, alkyd resins, chlorinated rubber, and they mix well with ethyl and benzyl cellulose. Though many waxes mix with coumarone resins, paraffin wax will neither blend nor mix.

Their combination with ethyl cellulose, polystyrene, and acrylates has interesting potentialities.

CHARACTERISTICS OF COMMERCIAL COUMARONE AND INDENE RESINS⁶⁴

Trade name	Type	Melting-point	Specific gravity	Refractive index	Acid value	General properties
Coumarone	Coumarone-Indene	..	About 1.1	1.630	Neutral	Suitable for oil and spirit varnishes.
Cumar	"	Different grades 5-170°	1.08	1.624	0.2	Soluble in all common solvents except alcohol and ethanalamine. Different grades used in rubber compositions and insulating materials, oil varnishes, printing-inks, N.C. lacquers and adhesives.
Neville	"	Up to 150°	1.04-1.15	1.60-1.65	Neutral	Soluble in hydrocarbons, ketones, and esters. Suitable for oil varnishes, chewing-gum, and rubber.
Nevindene	"	150-60°	1.04-1.15	1.60-1.65	"	Similar. Used for oil varnishes.
N.P.S.	"	100-5°	1.04-1.15	1.60-1.65	"	Soluble in oil at very low temperatures. Used in oil varnishes and chewing-gum.

REFERENCES

1. G.P. 392,002 (1917) and 394,217 (1923); U.S.P. 1,541,226 (1925); *Syn. App. Fin.*, 1935, 6, 135.
2. U.S.P. 1,263,813 (1918).
3. J. M. Weiss, U.S.P. 1,894,934; B., 1933, 929, and B.P. 338,845; B., 1931, 128.
4. I.G. Farbenindustrie, A.-G., B.P. 332,963; *Pat. J.*, 1930, 3842.
5. E. Stern, G.P. 345,816 (1919).
6. R. Stoermer, *Ber.*, 1897, 30, 1700.
7. E. Gläser, *Brennstoff Chem.*, 1921, 2, 115.
8. R. Stoermer and J. Boes, *Ber.*, 1900, 33, 3013.
9. R. L. Brown, *Ind. Eng. Chem.*, 1925, 17, 920.
10. *J. Amer. Chem. Soc.*, 1928, 50, 1160.
11. *Ber.*, 1891, 24, 3276; 1900, 33, 2257; 1901, 34, 1887.
12. H. Staudinger, *Ber.*, 1926, 59, 3032, and H. Stobbe and E. Färber, *Ber.*, 1924, 57, 1838.

13. J. Marcusson and E. Glaeser, *Brennstoff Chem.*, 1921, 113.
14. G.P. 310,785 (1918).
15. Schelber, *Farbe u. Lack*, 1926, 90.
16. G.P. 270,993 (1912), and 281,432 (1913).
17. G.P. 302,545 (1927).
18. U.S.P. 1,360,665 (1930), and B.P. 160,148 (1921).
19. B.P. 179,610 (1921).
20. B.P. 142,806 (1920), 160,148 (1920), and 225,216 (1925); G.P. 420,465 (1920); U.S.P. 1,360,665 (1920).
21. U.S.P. 2,047,245-7; B., 1937, 1374.
22. B.P. 142,806 (1920).
23. U.S.P. 1,353,220 (1920), and A. L. Tannehill, U.S.P. 1,389,791; *J. Soc. Chem. Ind.* 1921, 781A.
24. Capthorne, U.S.P. 1,389,791 (1921).
25. B.P. 166,818 (1920).
26. U.S.P. 1,395,968 (1921).
27. E. Gläser, *Brennstoff Chem.*, 1921, 99, 113; S. Masai, *J. Soc. Chem. Japan*, Suppl., 1933, 36, 583; B., 1924, 136; Neville Co., U.S.P. 1,990,215; *Chem. Abs.*, 1935, 29, 1903.
28. *Ind. Eng. Chem.*, 1938, 30, 245.
29. *Ibid.*, 1940, 32, 684.
30. *Ibid.*, 1937, 29, 576.
31. *Ibid.*, 1940, 32, 99.
32. *Ibid.*, 1938, 30, 1228.
33. U.S.P. 1,754,052 (1930).
34. U.S.P. 1,857,333 (1932).
35. *Ind. Chem.*, 1927, 431, 479, and B., 1935, 161.
36. *Artificial Resins*, translated by E. Fylemann (Isaac Pitman & Sons, Ltd., London 1931). See also *Kunst.*, 1919, 9, 190.
37. *Chem.-Ztg.*, 1919, 43, 109, 122.
38. By courtesy of M. E. Dougherty, London representative of the Barrett Co. See also T. H. Barry, loc. cit.
39. *Ind. Chem.*, 1927, 431, 479.
40. *Paint Manuf.*, 1933, 3, 259.
41. *Off. Dig.*, 1930, 93, 449; *Drugs, Oils, Paints*, 1930, 46, 20.
42. *Chem. Age*, 1939, 41, 397; and *Anon. Paint Technology*, 1936, 47; *Verfkroniek*, 1939, 12, 211; B., 1940, 53.
43. *Synthetic Resins and their Plastics*, New York, 1933, 54.
44. *Drugs, Oils, Paints*, 1929, 44, 297.
45. *Amer. Paint J.*, 1931, 15, 7.
46. G. Genin, *Rev. gén. Mat. Plast.*, 1934, 10, 10.
47. *Ind. Eng. Chem.*, 1920, 12, 549.
48. *Drugs, Oils, Paints*, 1929, 44, 297.
49. *Ibid.*, 1930, 46, 20.
50. *Ber.*, 1890, 23, 81.
51. Eichler, U.S.P. 1,133,432 (1915), Krumbhaar, *Farben-Ztg.*, 1916, 1086
52. U.S.P. 999,439 (1911); 999,708 (1911); 1,005,818 (1911); 1,381,863 (1922).
53. U.S.P. 1,157,768 (1915).
54. Carleton Ellis, U.S.P. 1,412,014 (1922).
55. J. P. A. McCoy, U.S.P. 1,299,847 (1919).
56. *Ind. Eng. Chem.*, 1928, 20, 198.
57. *Brit. Ind. Fin.*, 1932, 3, 156.
58. U.S.P. 1,038,475 (1912).
59. U.S.P. 1,268,031 (1918).
60. Power, U.S.P. 1,332,860 (1920).
61. U.S.P. 1,019,066 (1912).
62. U.S.P. 1,334,049 (1921).
63. Lender, B.P. 175,576 (1915); Rütgerswerke A.-G., G.P. 348,063 (1918), and J. R. Roether, U.S.P. 1,414,670 (1922).
64. A. Kuferath and E. R. Thows, *Paint Var. Prod. Man.*, 1933, 9, 23; A. W. van Heuckeroth and H. A. Gardner, A.P.V.M., Circ. 369 and 430; T. F. Bradley, *Ind. Eng. Chem.* (Anal. Ed.), 1931, 3, 304; D. R. Duncan, Tech. Paper 45, Res. Assoc. Br. Paint-Col. Varnish Manufs. (1933).

CHAPTER VIII

ESTER GUMS

By H. M. LANGTON

THE economic advantage of using rosin in varnish manufacture naturally encouraged attempts so to treat it as to reduce, if not entirely eliminate, those defects which rendered it unsuitable for use in oil varnishes. Rosin is very soft and has a low melting-point (70–100°) and a high acid value (145–185).

These defects are reproduced in any ordinary varnish containing a considerable proportion of rosin. In spirit varnishes the film is lacking in toughness and becomes tacky under the heat of the hand. In oil varnishes the same defects are present, and in addition the lack of resistance to moisture causes excessive 'blooming' even when the varnish is not actually exposed to weather. The high acidity of rosin, of course, makes it an undesirable ingredient of paint mediums to be used in conjunction with basic pigments. On the other hand, rosin is a powerful dispersing agent, and its presence in certain types of varnish is therefore beneficial, in that it increases the stability of the product. It also acts as a flux and facilitates the 'running' of the harder resins.

Its use in the paint and varnish industry is therefore not without justification apart from the question of price.¹

As a result of the efforts to produce a modified product, which shall possess the merits of rosin without its disadvantages, two types of product have been evolved.

(a) Ester gum in which the rosin acid is combined with glycerine.

(b) Hardened rosin in which the rosin acid is partly neutralized by a base, usually lime and less frequently zinc oxide or magnesia.

The first attempts to produce a hardened rosin by neutralizing with lime and other bases were those of A. Kissel.¹

Melvin² patented the production of ester gum by combining rosin with glycerine. He also included in his patent other highly acid resins such as Congo and Manila copals, and other basic substances such as phenols and carbohydrates.

These early attempts at making ester gum and hardened rosin do not appear to have been very successful, and apart from that the demand for them was not great. The position was, however, greatly altered by the introduction of China wood-oil in conjunction with which rosin proved a valuable varnish resin.

Of itself, China wood-oil is open to the objection that, even when heat-treated, it yields films which are inclined to web or wrinkle, due to the rapid gelation and oxidation of the surface of the film enclosing behind it the still liquid varnish which on setting expands and thus causes wrinkling in the surface layer.

Both ester gum and hardened rosin tend to promote gelation and, consequently, a more uniform setting of the film. Unchanged rosin has a similar effect, though not to so marked an extent, and apart from this its use is open to objection on the grounds already stated.³

The manufacture of ester gum and hardened rosin, therefore, received a great impetus when after the Great War the use of China wood-oil became firmly established in varnish manufacture.

Ester Gum.

The reaction between rosin and glycerine cannot in practice be carried to complete neutrality, nor does there appear to be any advantage in carrying the reaction beyond a certain point. As esterification proceeds the product becomes more insoluble in alcohol. H. A. Gardner and R. E. Coleman⁴ obtained the following results:

<i>Rosin ester</i>	<i>Acid value</i>	<i>Colour</i>	<i>Solubility in alcohol</i>
No. 1	158.9	Very pale	Soluble in cold alcohol
No. 2	119.6	Light colour, opaque	Soluble in cold alcohol, but cloudy partial solution
No. 3	27.4	Medium, opaque	Unaffected by alcohol
No. 5	17.2	Medium, opaque	Unaffected by alcohol
No. 6	8.18	Very pale, slightly cloudy	Softened, but not dissolved
No. 7	16.0	Dark brown, very hard	Unaffected

F. M. Beegle⁵ concluded that for practical purposes an acid value of 20 was sufficiently low to ensure good water-resisting qualities in an ester gum, and also stated that aluminium acted as a catalyst. Various other substances, such as zinc,⁶ have been suggested. It is also stated that the addition of 1½ gall. China wood-oil to every 100 lb. rosin accelerates the reaction. Gardner and Coleman (loc. cit.) found that China wood-oil facilitated the interaction of the glycerine and rosin, but this statement has been criticized. It is probable, however, that the function of the China wood-oil is merely to keep the ester gum in solution and thus facilitate the progress of the reaction. K. Pistor⁷ found that on prolonged heating a mixture of China wood-oil and rosin gave a certain amount of rosin glyceride, but it does not appear, however, that any rosin ester is formed at the expense of the China wood-oil in Gardner's experiment.⁸ In commercial practice catalysts are not generally used.

There has been an increasing interest in this problem during recent years as might be expected in view of the remarkable increase in the use of processes involving catalysts in industry. A. C. Johnston⁹ states that *p*-toluene-sulphonic acid is a catalyst for the esterification of rosin. Boric acid¹⁰ and hydroxy-aliphatic acids, such as lactic acid,¹¹ have been patented. The above catalysts are used to prevent the darkening of the rosin during esterification.

J. M. Schantz¹² states that incomplete combination between lime and rosin is frequently due to the presence of crystalline abietic acid, which does not combine satisfactorily with lime at any temperature

between its melting-point and 572° F. Calcium acetate acts as a catalyst, and the addition of 1 per cent. facilitates the reaction, and even when the crystalline acid is present pale products of satisfactory quality can be obtained. Other metallic acetates can be used but calcium acetate is to be preferred.

Mention may be made at this point of attempts to produce ester gums using alcohols other than glycerine. The methyl esters may be used as plasticizers. Improved fluidity, flexibility, and impact resistance of asphalt and increased speed of penetration into felt, paper, asbestos, and cellulose materials can be obtained through the use of liquid esters of abietic acid according to the Hercules Powder Company, U.S.A. (1941) whereby adhesion between asphalt and stone and gravel in road construction will result. The materials markedly reduce the viscosity of a blown asphalt at temperatures above its melting-point. The effect on viscosity is far greater than the reduction in the melting-point. According to K. Albert,¹³ rosin esterified with glycol yields resins of high water resistance.

The presence of 1 per cent. of zinc chloride or, less effectively, other inorganic catalysts, has been found by A. J. Kogan, N. N. Maharenko, and P. A. Sikar to facilitate the reaction between phenols and rosin, effected at 280–90° under a pressure of 10 atmospheres. Amongst various phenols examined, β -naphthol gave the most satisfactory varnish products, which were, however, in all cases slow drying. The rosins obtained are soft, and hardening is accompanied by loss in solubility in oils. The hardness, drying, and anti-corrosive properties do not compare favourably with copal varnishes.¹⁴

A. Fairbourne, G. P. Gibson, and D. W. Stephens¹⁵ have described the use of glycerylamines.

A general review of the recent methods for the hardening of rosin is given by H. Hardert.¹⁶

Successful manufacture of ester gums with a low acid value depends upon the correct adjustment of the condensing arrangements, so that water is allowed to escape, but glycerine vapour is returned to the melt. Using an open pot the acid value cannot be reduced to below about 60.¹⁷ Brendel, however, considers that the best results are obtained using an autoclave and maintaining the pressure at two atmospheres during the reaction. The autoclave is then evacuated and the temperature raised to 310–20° in order to harden the product.

In practice, an acid value of 10 to 13 is attained. Occasionally a small amount of lime is added to reduce the acidity, and it is therefore advisable to determine the lime content of samples for which a low acid value is claimed. According to W. Heart glycerol-colophony esters for weather-resisting varnishes must have an acid value less than 4–6 and be free from glycerol mono- and di-resinates. The use of a 1–2 per cent. excess of glycerol yields neutral esters.¹⁷

Murray¹⁸ recommends the addition of $\frac{1}{2}$ per cent. of quicklime in order to produce ester gums of very low acidity, the procedure advocated being as follows:

Six hundred pounds of rosin are melted in a copper or aluminium kettle at 204°, and to the melted mass 10 to 25 per cent. (72 lb.) of its weight of glycerine is added, and the temperature raised eventually to 290°, the optimum temperature, for 20 minutes until the acid value is reduced to 5 or 10. In order to reduce the acidity still further, $\frac{1}{2}$ per cent. of quicklime (3 lb.) is incorporated. In 1937 the production of ester gum in U.S.A. amounted to 35,000 tons (A. V. Blom).

Apart from the direct esterification, various other methods of obtaining products of superior quality from rosin have been suggested. E. Mossgraber¹⁹ dissolves the rosin in alkaline alcoholic solution and treats with an organic acid halide, e.g. acetyl chloride. The ester so formed can be distilled off and the residue, which is said to be a mixture of the anhydrides of the rosin acids and the lactones of the hydroxy-acids, is claimed to be specially suitable for use in insulating varnishes. F. W. Kressman states that superior products are obtained by esterifying the various fractions obtained by distilling rosin under reduced pressure.²⁰

The action of boron fluoride as a catalyst in the esterification of rosin²¹ and also on partly esterified rosin has been studied; moreover, the Hercules Powder Co. polymerize a Me. or glyceryl ester by stannic chloride, &c. to give a product which is oil-soluble.²²

The rosin is dissolved in a suitable solvent, such as solvent naphtha, and the boron fluoride, dissolved in cresol, added slowly over a period of 24 hours. On distilling the solvent, a resin is obtained. The effect in both cases is to reduce the acidity and the iodine value and to raise the melting-point. The patentees quote as examples of the reaction a case in which rosin was used and the acid value was reduced from 162 to 114, whilst with a partially esterified rosin of acid value 120 a product with an acid value of 58 was obtained. It is stated that damar and mastic can also be treated by these methods with useful results.

Distillation of rosin in the presence of Tonsil, a hydrosilicate, activated with hydrochloric acid for a short time at 205–15° yields a resinous substance, with a lower acid value, which is tougher and of higher melting-point than the original rosin, whilst action for a longer period at higher temperature²³ yields a pale almost neutral oil free from saponifiable matter.

The hardening of rosin by oxidation may be effected either by blowing air through molten rosin in the presence of a catalyst such as cobalt oxide,²⁴ or by oxidation in solution by means of ozonized air.²⁵

Products of these types are still in the experimental stage, and little appears to be known as to the chemical reactions involved or how the products will behave in practice, but it is evident that the natural resins, and particularly rosin, are capable of considerable modification by chemical means. At least some of the products may eventually become of practical utility.

In another patent by the I.G. rosin, xylene, and paraformaldehyde are kept at 30° for 8 hours, during which time boron

trifluoride is passed in. After dilution with xylene and decolorizing with fuller's earth a yellow clear resin is obtained with a melting-point 40° above rosin.

New rosin esters include also the glycol esters, described by G. M. Zilberman and R. Zamiuslov,³² and a product of the interaction of rosin acid with acetin protected by C. Dreyfus.³³

Henkel & Co.³⁴ have described the esterification of rosin or abietic acid, with phenolic compounds such as cresol, benzyl alcohol, hexanol, such compounds as butyl alcohol, chlorhydrins.

Vinsol resin is an oxidized colophonium esterified with alcohols or phenols to give a soft resin which serves as a plasticizer. Brit. Thomson Houston Co., Ltd. (B.P., 489,747; B., 1939, 177)²⁶ claim the production of resins of low power factor (with low rise with raised temperature), high dielectric strength, good resistance to oil, moisture and ageing, satisfactory hardness of film and flexibility; these are obtained by heating an oil-soluble phenolaldehyde resin with a Vinsol resin and a drying oil (tung oil and a heat-polymerized oil).

Reduced Abietate Resins.

In view of the oxidizability of rosin and its esters²⁷ the hydrogenated esters of resins are of interest. Staybelite or hydrogenated rosin gives lac films which show only a slight tendency to powder and to become yellow. I. W. Humphrey²⁸ esterifies abietic and pimaric or fossil resin acids with polyhydric alcohols and hydrogenates the esters, using a nickel catalyst at 250° . The new resins are recommended in place of rosin esters and fossil resins in varnishes and lacquers and they exhibit plasticizing properties. The development of cracking and yellowing is prevented. Other recent developments comprise a method of hydrogenating a rosin ester and its further reduction to a hydrogenated abietyl compound.²⁹ Acids such as acetic, phthalic, benzoic, ricinoleic, palmitic, citric, tartaric are stated to be suitable for solidifying hydrogenated abietyl alcohol for the production of esters, which may be used in coating compositions and in plastics.³⁰

Other Ester Gums.

A pentaerythritol rosin ester said to have a higher m.p. than the glycerol ester, but to be less soluble and to impart higher water- and alkali-resistance to varnish films has been described by T. Crebert.³¹

Satisfactory ester gums can be made from rosin, using instead of glycerol the hexahydric alcohols mannitol and sorbitol, by using 2.25 to 3 acid equivalents per molecule of the hexahydric alcohol. The ester gums thus produced³⁵ at $285\text{--}300^{\circ}$ according to R. M. Goepf, Jr., and K. R. Brown, have acid numbers less than 20, standard rosin colour G to H, and a softening-point between 120° and 140° (by ring-and-ball method) with properties intermediate between glycerol ester gums and modified phenolic resins. The hexitols can be incorporated with oil-modified alkyd resins.

In the preparation of these ester gums maintenance of intimate

contact between the hexitol and rosin is harder than with glycerol and rosin because of higher viscosity and greater density: very efficient stirring is essential not only to overcome these difficulties but to prevent local overheating.

It is best to mix at 120° and raise the temperature at the rate of 1° per min. up to a final 285-300°. Hexitols do not decompose to acrolein, though decomposition products are formed which are dark and this process is hastened by such impurities as metallic compounds, alkalis, alkaline earths, and iron.

The use of hexahydric alcohols or their inner ethers as esterifying agents³⁶ for rosin has recently been patented.

Coating compositions containing an ester gum may be obtained by reaction of rosin and erythritol $C_4H_6(OH)_4$ and pentaerythritol $C(CH_2OH)_4$ which have great hardness and elasticity (L. N. Bent, U.S.P. 2,066,759; B., 1938, 695).

Ester Gum in Cellulose Lacquers.

Ester gum is used largely in the manufacture of both clear and pigmented lacquers to which it is usually added in solution. Benzene or its homologues is largely used, but S. P. Wilson³⁷ recommends a mixture of 1 part ethyl acetate with 3 parts benzene. In clear lacquers the addition of more than 75 per cent. of ester gum, calculated on the pyroxylin content, reduces the hardness and adhesive properties of the film, but in pigmented lacquers higher proportions can be used depending on the extent to which the pigment hardens the film. The best results, however, are obtained by using ester gum in conjunction with damar, shellac, or coumarone.

Lime-hardened Rosin.

For the purpose of making lime-hardened rosin it is important to use a pure grade of lime practically free from:

- (1) Iron, which may cause discoloration;
- (2) Magnesia, which yields more insoluble resins than does lime, and which gives much more viscous solutions;
- (3) Calcium carbonate which does not react readily with rosin.

H. A. Gardner³⁸ suggests the following specification:

- (1) *Fineness*. Not more than 10 per cent. residue on a 250-mesh sieve.
- (2) *Magnesia*. Not more than 3 per cent.
- (3) *Iron, alumina, and insoluble*. Not more than 2 per cent.
- (4) *Carbon dioxide*. Not more than 2 per cent.
- (5) *Lime*. Not less than 70 per cent.

The use of slaked lime is to be preferred, as it is voluminous and finely divided, and therefore reacts more readily with the rosin.

The reaction between lime and rosin takes place vigorously at above 260°, and Gardner therefore suggests that a practical test should be carried out on samples of lime as follows:

Fifty grammes of rosin are heated to 180° and 2 gm. of lime added. The temperature is then raised to 260° and cooled to 205°, when the melt is thinned with 50 gm. white spirit. The rate of reaction, the clarity of the product, its acid value, and its stability are noted.

In practice it is not possible to neutralize the rosin entirely, nor is this desirable, as a too heavily limed rosin tends to become insoluble, and owing to the incomplete combination is invariably cloudy due to the presence of lime in suspension.

An acid value of from 60-20 is usually aimed at in practice.

In making gloss oils it is also important to select a suitable grade of thinner, as white spirits of different origin and composition differ in their solvent power for ester gum.

'Gloss oils', made by dissolving lime-hardened rosin in linseed oil and thinning with white spirit, are used as media in very cheap enamel finishes for articles, such as toys and containers for confectionery, &c., which are not exposed to weather and in which durability is not of importance. With an increase of the ratio of hardened rosin to oil the gloss is increased and the elasticity reduced. Usually the ratio does not exceed equal parts of hardened rosin and oil, but as much as 5 parts of hardened rosin to one part of oil is sometimes found in cases where a quick-drying high gloss finish is required and neither elasticity nor durability is of material importance.

The Use of Other Metals.

Zinc oxide is sometimes used to neutralize rosin, especially for use in grinding varnishes.³⁹ It is, however, better used in conjunction with lime in the ratio of about 4 parts of lime to 3 parts of zinc oxide.

Esterification of Other Resins.

As already stated, the esterification of resins other than colophony was suggested by the earliest workers, but the production on a commercial scale of esterified copals is of comparatively recent development. The difficulties in producing these substances were mainly associated with the temperature control of the viscous mass and the correct heat-treatment of the resin prior to esterification. Unless decomposition by heat has proceeded to a sufficient degree, the reaction with glycerine is somewhat violent, and the resin polymerizes, forming a spongy useless mass.⁴⁰

The use of a mixture of rosin and copal is the obvious solution of the problem and indeed would appear to be an advantage in that the esterified copals are more prone to gelation than ester gum, and consequently the presence of the rosin ester would increase the stability of the product. Murray⁶ found that a mixture of 1 part rosin to 3 parts copal gave on esterification a product with an acid value of 7.5 which gave satisfactory varnishes. He suggested that the polymerization might be induced by the copper vessel used acting as a catalyst. Gardner and Holdt, however, obtained the

same results using glass vessels. W. J. Pearce, R. Carlson, and C. S. Rydstrom⁴¹ in a general survey of the subject state that aluminium is a catalyst for the esterification of Congo copal, but not for Manila copal, and further that the aluminium does not have any catalytic effects if a monel metal pot is used. As the resin alone does not polymerize when subjected to the same heat-treatment, and polymerization does not occur when the resin is completely run, it appears that the presence of compounds in the resin which have escaped complete decomposition during 'running' are responsible for the polymerization. Manila and Pontianak copals behave in a similar way to Congo copal.

Improvements in plant and methods of temperature control have enabled the manufacturer to esterify Congo copal without the addition of colophony, and during recent years rosin-free copal esters have come on the market, though for general use an ester containing a small percentage of rosin is satisfactory.

The rosin-free type of copal ester is claimed to be the hardest varnish resin known. The acid value is from 10 to 14. These ester copals have the advantage over synthetic resins in that they do not cause yellowing of white enamels. Although they do not require running in order to incorporate them with the oil, it is necessary that the mixture should be well cooked in order to ensure stability of the varnish. In this respect they resemble the harder types of 'Albertol Resins'.

Owing to their low acidity copal esters do not cause livering when used in media for enamels containing basic pigments. As in the case of rosin, esterification greatly increases the resistance to alkali. Gardner and Holdt⁴⁰ found that an ester copal varnish was unaffected by immersion in 16 per cent. caustic soda for a week. A. Mann⁴² found that Congo esters yielded varnishes which were superior to those from synthetic resin in durability, and had the advantage that they did not yellow with age. Copal esters may be condensed with polybasic organic acids to give Beckopols or with alkyd resins. Congo copal esters may be used as press materials, which by plasticizing with linseed oil or castor oil provide a high degree of resistance to mineral oil.

At the present time colophony and Congo copal are the only natural resins which are esterified on a commercial scale. There is no reason, however, why Manila copals and Kauri should not be similarly treated, but the relatively low price of Congo copal is the determining factor, as there does not appear to be any advantage from the technical point of view in using the other copals. A glycerol ester of Kauri with an acid value of 10 is stated to possess a high melting-point. Kauri ester yields a more viscous solution in linseed oil than does Congo ester.⁴³

It is stated⁴⁴ that damar can also be esterified with advantage, the tackiness and lack of elasticity characteristic of damar varnishes being eliminated. Carleton Ellis,⁴⁵ however, failed to obtain satisfactory results on attempting to esterify damar, the main objection

being the very dark colour of the product. It should be noted, though, that whereas H. Brendel recommends the use of only 2 per cent. glycerine, Carleton Ellis found it necessary to use 10 per cent. glycerine and to continue the heating for half an hour at 250° when the acid value fell from 39 to 12.5.

It has been known for some time that rosin can be esterified with shellac, but the esterification is incomplete and the acid value of the product high, and the resultant esters are not compatible with drying oils. R. Bhattacharya⁴⁶ now reports that recently it has been found possible to esterify rosin almost completely with shellac, and the esters are compatible with drying oils and are soluble in hydrocarbon solvents.

In the reaction, the lac plays the part of a polyhydric alcohol (two hydroxyl groups of the five present in the molecule are reactive), an ester gum of rosin being formed in effect. The difference between glycerol-ester gum of rosin and lac-rosin ester lies mainly in the more complex molecular structure and magnitude of the latter, according to Bhattacharya.

When rosin and lac are heated together at 220° and the temperature raised to 275° (castor oil being added during the cooling and reacting chemically with the lac-rosin ester subsequently formed), two reactions appear to proceed simultaneously:

(a) esterification of the (HO) groups of the lac with the (COOH) groups of rosin, and (b) a mutual reaction between the (HO) groups of lac. This second reaction induces the polymerization of lac and causes gelation of the mixture. This reaction can be delayed or inhibited by the presence of excess of rosin. The added castor oil retards the gelation sufficiently.

It is claimed that the paints made from this type of rosin show excellent weathering properties, even without drying oils. The acid value is low and the varnish can be baked. When the usual driers are added, varnishes drying in 6 hours can be made.

The behaviour with linseed oil is anomalous: the lac-rosin extended with linseed oil takes longer to dry but a non-tacky film is possible, particularly on pigmentation. Extension with tung oil, even on cooling for 30 min. at 270°, gives a film remaining tacky for several days, which is contrary to the usual behaviour of tung oil in varnishes.

During the last few years a number of papers have been published which put forward a rehabilitation of natural resins. Advocates of the natural resins contest the belief that certain outstanding properties would make synthetic resins generally applicable to every possible purpose. At the present moment there is once again a clear understanding that varnish manufacture is a matter of compromise, and that in the resin field there is ample room for both products, the synthetic resins and the natural gums. The ester gums are examples of such a compromise, and good quality ester gum occupies a position in the varnish industry surpassing all other resins. Nevertheless, it must not be considered as a competitor of synthetic resins, but rather a desirable material to cheapen and extend synthetic

products, imparting to them some valuable technical properties, gloss, solubility, &c. Improvements in the quality of ester gums, e.g. lighter colour, lower acid value, higher melting-point, have been achieved by refinement in apparatus, which permits complete control of the process: such is the statement by W. Krumbhaar.⁴⁷ He refers to methods of processing normal ester gum (tri-abietaate) to increase its reactivity and plasticity with vegetable oils which can be effected either by treatment with polybasic carboxylic acids, with formaldehyde polymers, or with phenol-formaldehyde condensation products, &c. In the treatment of the ester with a straight formaldehyde condensation product at approximately 500° F., even as little as 20 per cent. of phenolic condensation product is sufficient to raise the melting-point as much as 40° F., and will increase its viscosity considerably, but, as experience has shown, this process is best carried out by the manufacturer of synthetic resins inasmuch as the products are more uniform, more soluble, and lighter in colour. Reference may be made to a communication by G. Dring⁴⁸ and to patent literature.⁴⁹ Krumbhaar (loc. cit.) gives a most interesting account of recent advances made in the treatment of natural resins for varnish purposes.

Meister⁵⁰ reviews the application of copal esters and claims that copal esters can replace rosin esters and synthetic resins in recipes. The esters are heat resistant and can be used in the American process of varnish making, in which the resin is heated with tung oil to about 280° and quickly cooled with polymerized linseed oil.

The attack of the synthetic resins on the resin or copal products has stimulated investigation of the properties of the latter. In the shellac industry there is the same resistance to the pressure of the synthetic resins as shown in the results obtained by the London Research Bureau and other lac research organizations (*Annual Report of Shellac Research Bureau*, 1940). Shellac will combine with the monoglycerides of unsaturated fatty acids to yield varnishes in a similar manner to that of copal resins.⁵¹ Ethylene-glycol ethers of lac have been obtained by the reaction between the hydroxyl groups present in glycol and lac. These ethers have been esterified further with acids, and new and interesting compounds have been obtained. Heat polymerization of the glycol-ether of lac has resulted in elastic and rubber-like compounds which seem to possess molecular weights of about 22,000. The formation and properties of these new lac derivatives appear to agree with the generally accepted theories of polymer formation (cf. Chapter XVI, p. 498). Though further study of the physical and electrical properties of these ethers and ether esters will be necessary before definite recommendations can be made as to specific uses, the preliminary study indicates possible industrial applications. The breakdown voltages of these compounds is high; the polymerized products resemble rubber physically. There is a considerable demand for flexible insulating materials (for cables, &c.) which can withstand the action of ozone. Further, these compounds, when fully cured, are rubber-like and at the same time insoluble in

solvents and vegetable and mineral oils. It is possible to impregnate textiles and other suitable materials with them for use as packings or jointings for special purposes. The coating is non-tacky and does not require a tack-removing coat. The process is simpler and quicker than that of processing silk with drying oils. These treated fabrics, apart from the ordinary waterproof clothing, may be used as anti-gas and perhaps parachute fabrics, and minor uses are indicated in the formulation of paints for elastic surfaces, as a plasticizer for lac, and in leather finishes. The unpolymerized compounds may be used as special adhesives. The investigation has been carried out by B. S. Gidvani and is described in detail in the London Shellac Bureau, Technical Paper, No. 17.

It is impossible here to discuss further the modifications of shellac, but mention must be made of the heat-curing of shellac and removal of the soft resin by weak alkali to give sclerolac⁵² which is now a commercial proposition in Great Britain, U.S.A., and Europe.⁵² Improvements in grading, uniformity, and in running of copals, and fuller investigation of the rosin complex will go far to restore the prestige of the natural products and enable them, as Krumbhaar points out, to be used efficiently in combination with synthetic resins.

REFERENCES

1. G.P. 30,000 (1884), and U.S.P. 303,436 (1888) and 413,336 (1890).
2. U.S.P. 370,640 (1887).
3. Schlick, *Farben-Ztg.*, 1922, 27, 1439, 1511, 1583, and 1650.
4. A.P.V.M., 1920, Circ. 101.
5. *Ind. Eng. Chem.*, 1924, 16, 953 and 1075.
6. S. P. Murray, *Chem. & Met. Eng.*, 1921, 25, 493, and F. W. Stirling, V. E. Grotsch, and F. B. Veitch, U.S.P. 1,395,874 (1921).
7. *Farben-Ztg.*, 1925, 30, 3056.
8. Ragg, *Farben-Ztg.*, 1921, 26, 2335.
9. U.S.P. 1,840,395; B., 1932, 1042.
10. I.G. Farbenindustrie, A.-G., G.P. 581,956 and 577,691.
11. I.G. Farbenindustrie, A.-G., U.S.P. 1,940,092 (1934).
12. *Paint, Oil, & Chem. Rev.*, Oct. 22nd of 1931.
13. G.P. 509,368 and *Rev. Prod. Chim.*, 1932, 35, 49.
14. *Farbe u. Lack*, 1934, 207, 218, 232; B., 1934, 590, and *Oil Col. Trades J.*, 1935, 88, 103.
15. *J. Soc. Chem. Ind.*, 1930, 49, 1021, 1069.
16. *Paint Varn. Prod. Man.*, 1935, 16.
17. H. Brendel, *Farben-Ztg.*, 1926, 31, 576; W. H. Heart, *Metallborse*, 1934, 24, 1162; B., 1935, 599.
18. *Chem. Met. Eng.*, 1921, 25, 475.
19. B.P. 367,874; B., 1932, 475.
20. B.P. 354,332; B., 1931, 936.
21. I.G. Farbenindustrie, A.-G., G.P. 564,897 (1931), and G.P. 425,366.
22. I.G. Farbenindustrie, A.-G., G.P. 575,132 (1931), and B.P. 399,206, 399,211; B., 1933, 1021; U.S.P. 2,154,704.
23. I.G. Farbenindustrie, A.-G., G.P. 572,474 (August 1931).
24. E. Schaal, G.P. 419,673 (26/7/24), see also G.P. 128,034 (1900).
25. A. P. Ramage, U.S.P. 1,752,693 (1930); B., 1931, 128. See also G.P. 434,419 (1922) (A. Riebeck'sche Montanwerke A.-G.).
26. B.P. 489,747; B., 1930, 177.
27. R. S. Morrell and E. O. Phillips, *J. Soc. Chem. Ind.*, 1940, 59, 144 T.
28. I. W. Humphrey, U.S.P. 2,051,796; B., 1938, 193.
29. U.S.P. 2,187,576.
30. U.S.P. 2,130,740.
31. *Fette u. Seifen*, 1930, 46, 287; B., 1939, 746.
32. *Za Lakokras. Ind.*, 1935, No. 1, 23.
33. Can.P. 351,420 (1935).
34. F.P. 785,486 (1935).
35. *Ind. Eng. Chem.*, 1938, 30, 1222.
36. U.S.P. 2,134,430 (1938).
37. *Pyroxylin Lacquers and Enamels*, Constable, London, 1928, p. 88.
38. N.P.V.L. (U.S.A.), Circ. 113 (1921).

39. Carleton Ellis, *Synthetic Resins and Their Plastics*, p. 263.
40. H. A. Gardner and P. C. Holdt, N.P.V.L. (U.S.A.), *Circs.* 151; 270.
41. *Ind. Eng. Chem.*, 1927, 19, 285.
42. *Farbe u. Lack*, 1934, 146, 158; *Paint Res. Stat. Rev.*, 1934, 215.
43. J. R. Hosking, New Zealand, *J. Sci. Techn.*, 1935, 17, 369.
44. H. Brendel, *Farben-Ztg.*, 1924, 29, 1693.
45. *loc. cit.*, p. 282.
46. *J. Oil Col. Chem. Assoc.*, 1940, 23, 145.
47. *Ibid.*, 1934, 17, 416.
48. *Chem. Ind.*, 1934, 1013.
49. I.G. Farbenindustrie, A.-G., G.P. 578,570 (1933); also G.P. 582,846, 582,848, and 584,967 (1933).
50. *Farben-Ztg.*, 1934, 39, 753; B., 1934, 803.
51. R. Bhattacharya and B. S. Gidvani, *J.S.C.I.*, 1938, 57, 285 T.
52. M. Rangaswami and R. W. Aldis, *Ind. Lac. Res. Inst.*, 1934, Bulletin 19.

CHAPTER IX

PHENOLIC RESINS IN OIL VARNISH AND ENAMEL MANUFACTURE

By H. S. LILLEY

THE resins produced by the interaction of ordinary phenol and mixtures of cresols (as used in plastics manufacture) with formaldehyde are soluble (in their A stage) in alcohols, ketones, and similar solvents, and the solutions have some tolerance for aromatic hydrocarbons, but little or none for the aliphatic thinners, such as are generally used in paint technology. The solutions which are possible yield either air-drying or stoving films according to the method of manufacture of the resin (generally according to the nature of the catalyst and the molecular proportions of phenol and formaldehyde).

Acid catalysis leads to air-drying but permanently fusible films, while alkaline catalysts are more generally used for stoving and heat-hardening materials. Such alkaline catalysts are generally neutralized on completion of resin formation. Air-drying films, though hard, are generally brittle, and the stoving films require a special technique in their application. Brush application is generally impossible and spray application is difficult. All these films show poor adhesion to metal, poor durability, and severe yellowing on exposure to the weather. On the other hand, they have outstanding resistance to corrosion, chemical action, and to certain solvents. Such products are, therefore, normally not suitable media for normal paints such as are used in the decorative field. They have, however, certain limited uses in the industrial field where corrosion or solvent resistance is essential so that application difficulties are repaid. The products also have value as insulating varnishes, as is discussed in Chapter XIV.

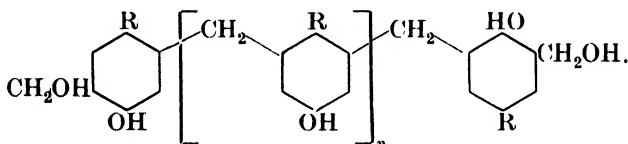
The properties of this type of resin, which are generally called 'spirit-soluble' phenolics, are discussed in more detail later. Sufficient has been said, however, to indicate that they are of no general use in paint technology. This conclusion is reinforced by the insolubility of these resins in drying oils. The varnishes forming the bases of enamels consist essentially of natural resins cooked into drying oils at high temperatures and subsequently thinned with hydrocarbons. No such process is possible with the simple Novolac and Resol resins hitherto considered.

The extensive use of phenol formaldehyde resins in paint technology followed the development of resins of this type which were soluble in drying oils. In this development three main stages may be distinguished:

- (1) Modification of the products with natural resins, a process dating back to 1912-14 and largely associated with the names of K. Albert, E. Fonrobert, and their associates.

- (2) Processes involving the heating together of selected phenols, drying oils, and formaldehyde. This process is associated with H. H. Morgan and his collaborators, and dates back to about 1928. A somewhat similar process is one in which drying oil and phenol are reacted together followed by treatment with formaldehyde, this reaction being largely worked out by members of the staff of the Bakelite Corporation. For reasons discussed later the processes of method (2) lie rather outside normal varnish-making practice.
- (3) The development of resins by the interaction of formaldehyde with phenols so selected with respect to chemical structure that the resulting resins are soluble in drying oils. These products are largely associated with the names of H. Hönel, the firm of Beck, Koller, and workers associated with the Bakelite Corporation. This development dates back to 1929.

The products of group (3) constitute the so-called '100 per cent. phenolics' of commerce. It can be said that the resins are regarded as consisting in a chain of phenolic molecules joined by CH_2 groups (the number of such molecules being probably about seven), with a variable proportion of hydroxymethyl ('methylol') groups. The general formula is therefore:



This represents the resins given by di-reactive phenols; for tri-reactive phenols cross-linking is possible, and no general formula can be given. These resins are oil-insoluble and require treatment to give soluble resins. A useful and concise statement of the above structures has been given by N. J. L. Megson.¹

Phenol-formaldehyde resins can also be obtained in forms suitable for paint and enamel manufacture by interpolymerizations with alkyd and styrene resins, as will be discussed subsequently.

The above types of oil-soluble phenol-formaldehyde resins will be discussed separately, but before doing so certain general considerations may be put forward with advantage.

There is now a considerable sale of these products which possess undoubted technical advantages to be considered later. It is claimed by the makers that the products, being synthetic and produced under controlled conditions, are *ipso facto* superior to the earlier natural resins, which were often crudely collected and badly graded. This is, of course, only a partial truth. There are possibilities, for instance, in congo-linseed oil systems which cannot be matched by any synthetic resin so far developed; the deficiencies of phenol-formaldehyde resins with respect to linseed oil have not yet been overcome.

The advent of the newer types of phenol-formaldehyde resin stimu-

lated research into the structure of natural resins so that, thanks to various workers (notably Ruzicka, Stock, Hosking, Mertens,² and Hellinckx³), we have a fair idea of their structure also. Such information concerning the structure of natural resins should be kept in mind, since many phenol-formaldehyde resins are modified with these and the natural component of such a modified resin will have its own reaction and behaviour towards drying oil. This is especially true of rosin-tung oil systems.

It is also generally and widely held to be a distinct advantage that we have some idea of the structure of oil-soluble phenol-formaldehyde resins, especially of type 3 mentioned above. There has in consequence been considerable work (discussed later) on the mechanism of formation of varnishes in which these resins are used. In all this work the structure and behaviour of the oil used in varnish-making has been too much neglected. Such neglect is manifestly unreasonable. The phenol-formaldehyde resins have low molecular weight, are generally incapable of cross-linking, and have poor durability. The polymerized oil is also of low molecular weight, but is highly cross-linked and fairly durable. Since the resulting varnish is durable and has many other properties not compatible with the above facts, it follows that some kind of reaction must have occurred during the process of varnish manufacture. Such reactions can only be properly understood and the phenol-formaldehyde varnishes correctly formulated if the structure of oils used is kept in mind, as also their behaviour on polymerization. It should particularly be remembered that natural resins are generally either acid or neutral, whereas the synthetic resins are either neutral or alcoholic, so that the two types will behave differently with respect to a given drying oil.

It is the experience of the writer that in publications on oil-soluble phenol-formaldehyde resins and their use the function of the drying oil is too much neglected, far too much emphasis being placed on the properties and virtues of the synthetic resin. This attitude applies especially to resins of type 3, many of which react in an obvious way with drying oils, so that they are called 'oil-reactive'. Most probably all oil-soluble phenol-formaldehyde resins, as will be seen later, are oil-reactive in some sense. This being the case, intelligent users of these products must bear in mind the structure of the drying oils used and the structure of the materials such oils give on polymerization by heat or on oxidation.

This is clearly not the place in which to discuss an admittedly involved matter in any detail, but some brief statement seems to be advisable in view of the above contentions. The only oils used in conjunction with phenol-formaldehyde resins are the true drying oils, namely, tung oil, dehydrated castor oil, linseed oil, and perilla oil, either raw, heat-treated, or blown. These oils subdivide readily into two classes:

- (1) Those containing conjugated linkages, namely, tung oil⁴ and dehydrated castor oil,⁵ although recent work has thrown some doubt as to the degree of conjugation of the latter.⁶

- (2) Those not containing conjugated systems, namely, perilla and linseed oil.

It is clear that a given resin will behave differently towards oils of types (1) and (2) if only on the grounds of the Diels Alder changes which are possible in one case and not in the other. This is borne out by the fact that phenol-formaldehyde resins behave very differently in respect to tung oil and linseed oil. Linseed oil varnishes containing this type are generally not very successful, and most phenol-formaldehyde varnishes contain some tung oil.

These two types of oil further behaved differently on heat treatment, and in the preparation of the varnishes under consideration high temperatures, 230–300°, are often employed for prolonged periods. On polymerization type (1) principally undergoes some kind of modified Diels Alder transformation leading to six-membered rings, as was suggested by Kappelmeier,⁷ Jordan,⁸ and other workers. This view is not clearly proved, but the recent work of Farmer and Morrison-Jones⁹ on methyl sorbate tends to prove the truth of this view. With type (2), on the other hand, there is first a gradual shift of double bonds to give conjugated systems, which then polymerize as for type (1). This view was first put forward by Scheiber¹⁰ and has been largely substantiated by later workers.¹¹ It is to be noted that, speaking very generally, the polymers are of low molecular weight and principally dimeric.¹²

For a full discussion on the above ideas the readers should consult the work of Long, Morrell and his co-workers, Blom, Kappelmeier, Scheiber, Rossmann,¹³ and many others. It should be borne in mind that the Kienle concepts of polymerization (which are discussed elsewhere in this book) can also be applied to drying oils, this having been done by Kienle¹⁴ himself as regards oxidation and since (by Bradley¹⁵ and his associates) as regards polymerization.

Most of the work cited above deals especially with chemical changes occurring on heat treatment, but the problems have also been treated more from a physical viewpoint by W. E. Wornum.¹⁶ Enough has, however, been said to indicate that the use of phenol-formaldehyde resins in varnish manufacture must always be considered in conjunction with drying oil, which is a highly complex and reactive body undergoing changes under heat during the preparation of the varnish. The nature of this complex body and its subsequent changes cannot, therefore, possibly be neglected.

Modifications with Natural Resin.

In 1912, only a short time after the development of phenolic resins by Baekeland, oil-soluble resins of this type were produced in Germany. This was done by suitable incorporation of natural resin, usually rosin.¹⁷ In early work phenol, formaldehyde and rosin were combined together,¹⁸ and later pre-formed resins were treated with acidic natural resins.¹⁸ Later there followed processes of esterification such as are used in the manufacture of ester gum, so as to improve

durability. The number of processes of this type which have been described is very great. There is, none the less, great uncertainty as to how many of the more successful commercial products are actually made. The new products first appeared as Albertol copals, this title being chosen to distinguish them from ester gums. The name is, however, unfortunate, as the products bear no relation to fossil copals. There is a tendency for the name 'Albertol' to be used generically for this type of resin.

After the War of 1914-18 there arose a need for quick-drying varnishes having satisfactory durability, and such products could not be obtained with the linseed-oil copal products then available. The development of industrial nitrocellulose no doubt stimulated this demand. There was also a desire to avoid the prolonged ageing and 'tanking' periods necessary with the orthodox gum varnishes; this can be done with the synthetic products. At the same time tung oil became more freely available, and this oil proved to be especially useful in conjunction with the new resins but difficult to work with fossil gums. It can in fact be argued that oil-soluble phenol-formaldehyde resins would never have been successfully developed without available tung oil.

From this time, therefore, the development of these resins has been continuous and successful, and rosin-modified phenol-formaldehyde resins are now marketed by many firms. The products are available under such trade names as Albertol (Amberol in America), Bakelite, Beckacite, &c. All these trade names, however, do not refer to resins of the type under discussion as is sometimes thought. Thus, Albertol 142R is a '100 per cent. phenolic' and Beckacite 1110 is a rosin-maleic acid product. The chief products commercially available are shown in the attached table (p. 273). Products of this type are generally made from the phenol and cresol mixtures readily available and which do not give oil-soluble resins without modification. The defect of poor light-fastness usually associated with the use of these phenols is not marked, as the proportion of phenolic constituent is generally quite low. The beneficial effect of the phenolic component is quite disproportionate to the amount of phenolic constituent. The proportion of phenolic component probably cannot exceed a moderate figure, as only products with excess rosin can be esterified with glycerol.

Little information has been published concerning possible reactions between the phenolic component and the rosin. Some considerations have recently been advanced by Sleightholme.¹⁹ This author points out that rosin is essentially a monocarboxylic acid with conjugated double-bond system, while the phenolic resin contains alcoholic groups. Three reactions, therefore, are possible:

- (1) Between the alcoholic and carboxyl groups.
- (2) Between the alcoholic group and the conjugated system.
- (3) Between the phenolic group and the carboxyl group.

The author regards the second reaction as the more likely. The phenolic rosin complex so formed reacts further with drying oil on

cooking, as has been recognized since 1928.²⁰ Ester interchange is now regarded as a principal feature of this reaction.¹⁹

The most suitable methods of using rosin-modified phenol-formaldehyde resins to give useful varnishes are best obtained by a critical consideration of the technical literature put out by the vendors of these resins. The number of processes described is so great that any adequate summary is impossible. There are also many technical papers on this subject, the chief of which are cited below.²¹ Generally, however, these are not all of very high quality and do not compare, for instance, with the work of Turkington and his associates on straight phenolic resins and derived varnishes (*vide infra*).

The use of Albertols with drying oils has developed along different lines in Germany and America, and there are distinct cooking techniques involved. America favours high temperatures and short times, Germany favours low temperatures with longer times and the use of bodied oils. It appears that the final products are, however, closely comparable.²² Workers in this field should not neglect the special conditions of time and temperature necessary to secure complete compatibility of drying oils with hard resins such as Albertol 209 L.²³ The high proportions of tung oil used make it necessary to ensure that the oil is properly 'cured' or 'gas-proofed'. These resins, both from viewpoints of their phenolic and their rosin component, are very suitable for this purpose.

The quick-drying ('four-hour') varnishes obtained by the use of these resins are quite durable, thus distinguishing them from the short oil congo varnishes previously extant.

The main principle to be observed is that some tung oil should be used if at all possible, and this should be combined with a resin first, linseed oil being added afterwards, preferably as stand oil. The limitations of these resins as regards linseed oil apply as with the 100 per cent. phenolics, though not to so great an extent. The varnishes so obtained can be thinned with white spirit, there not being the limitations in this respect which surround certain '100 per cent. phenolics'. Low proportions of driers can be used.

The special potentialities of phenol-formaldehyde resins with respect to tung oil have been summarized by F. J. Siddle,²⁴ who follows Thomas and Marling²⁵ on the effect of phenols in accelerating the polymerization of tung oil.

Recognizing the difficulties inherent in phenol-formaldehyde linseed oil combinations the Bakelite Company have recently introduced their phenolic resins BR. 2963 (which is rosin-modified) and R. 10825 to be used in conjunction with linseed oil.

Natural resins other than rosin can be used as modifying agents. A valuable product can be obtained by the combination of phenol di-alcohols or lightly condensed resin with fossil gum.²⁶ The gum may be run first or to preserve colour can be alternatively subjected to a process of mastication.²⁷ Resins of this type such as Beckapol 1400 are especially suitable for hard varnishes, rubbing varnishes, and the like.

The extensive publicity which has been given to the 100 per cent. phenolic resins may appear to have driven the products described in this section somewhat into the background. It is most doubtful, however, if this has in fact been done. Such relegation could not be justified, as these resins give very satisfactory results for general purposes, especially when their low cost is considered. The more expensive resins are probably only justified when certain special requirements such as outstanding corrosion resistance or light-fastness are required. The 'Albertol' type has not developed so much in the decorative field as might have been hoped owing to the outstanding success which has been achieved by oil-modified alkyd resins. They have, however, wide application in the industrial field both for air-drying and stoving products where high durability and resistance to adverse conditions are especially required. They also have a considerable use in wire enamels, in insulating varnishes, spar varnishes, and in other specialized uses.

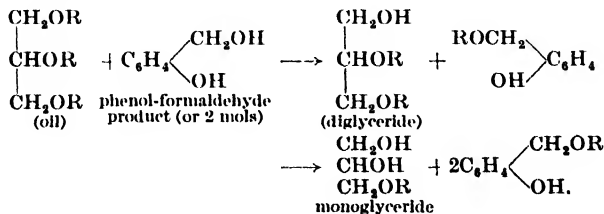
Modifications with Drying Oils.

Preliminary work in this field was carried out by Brown,²⁸ who heated together bodied driered tung oil with cresol and formaldehyde, and who studied other like processes.

The main developments are, however, associated with workers of Imperial Chemical Industries and the Bakelite Corporation.

The methods adopted according to the patents of the latter group²⁹ consist in heating together phenols with drying oils (when reaction probably occurs) followed by treatment with aldehyde, with or without other modifying agents.

In the processes developed by the former group drying oil, a phenol and aldehyde are heated together, with or without catalyst or solvent.³⁰ The catalyst (generally alkaline) affects the course of the reaction and the nature of the product. The higher phenols present in coal-tar, such as mixed xylenols, are especially suitable for use in these processes. There are limitations as to the drying oil which can be used, but tung oil is especially useful. It is supposed by H. H. Morgan³¹ that a process of ester interchange or 'alcoholysis' occurs between the resin and the oil during the formation of these resins.



Formaldehyde then reacts with (1) phenolic group of $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CH}_2\text{OR} \\ \diagdown \text{OH} \end{array}$,
 (2) with the monoglyceride (cf. acetal reaction, p. 470).

The oil-modified products obtained by the methods of this section are entirely distinct from products of the same ultimate composition obtained by cooking pre-formed resin into drying oil, being of the nature of varnishes and not of resins.

The oil-modified phenol-formaldehyde resins are especially of value in durable corrosion-resistant industrial finishes. They have little use in the decorative field, as they do not air-dry readily. Their chief defect is that of colour changes on stoving or on exposure.

100 per cent. Phenolic Resins.

In view of the general lack of durability associated with rosin it is natural that attempts should be made to prepare oil-soluble resins free from this component. This has been accomplished by the use of suitably selected phenols. These are such as are para-substituted so that the resins are long-chain polymers and permanently fusible. The products are nearly always oil-soluble also, but the reasons for this have not been fully elucidated.

A recent review by F. Seebach³² does not advance matters greatly. The substituent group is supposed to have considerable effect, but it is doubtful if this is the case, as this group can range from methyl to phenyl. The essential simplicity of the resins (only one isomer to a given polymer is possible, so that a kind of polyhomologous series is produced), and the inevitable availability of the methylol groups for ester interchange seem to be of more importance.

The raw materials principally used in the manufacture of these resins are para-hydroxyl diphenyl ($p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{OH}$)³³ and para-alkylated phenols. The former is a by-product of the synthetic phenol industry. The latter are produced by the interaction of phenol with olefines and secondary and tertiary alcohols,³⁴ these being in turn derived from natural gases. The development of all these products is essentially American.

It may, however, be mentioned that oil-soluble resins can be obtained from xylenol mixtures³⁵ if low formaldehyde/xylenol ratios be observed and ammonia be used as catalyst. This limitation does not apply to the phenols mentioned above. With high ratios of formaldehyde the oil-soluble resin from the tri-reactive meta-5-xylenol will cause difficulty. The oil-solubility of resins from this phenol remains unexplained. The remaining five-xylenols are, of course, mono- and di-reactive. The xylenol resins give very durable varnishes but are unfortunately not very light-fast.

The properties of 100 per cent. phenolic resins (in addition to their oil-solubility) are largely determined by:

- (1) The nature and amount of the catalyst used in their preparation. The catalyst is invariably basic in character, as the resins must be of the phenol alcohol type, but the degree of basicity affects the product.
- (2) The molecular ratio of formaldehyde to phenol. This determines the proportion of methylol groups, and hence the

'oil-reactivity'. The proportion of catalyst also affects this proportion, so that (1) and (2) are linked together. This is because the proportion of catalyst affects the molecular weight,³⁶ increasing amounts increasing this, so that the percentage of methylol (necessarily attached to the terminal rings of the molecule) falls off. This is one of the few known cases of effect of catalyst on molecular weight for condensation reactions. The effect is well established for polymerizations such as that of styrene.

The mechanism of formation of these resins has been discussed, particularly by Hönel.³⁷ It should be noted that formaldehyde is eliminated as the polymerization of these resins proceeds.

The properties of varnishes from hydroxy-diphenyl resins have been the subject of a series of papers of considerable value which are discussed later. The varnishes show great resistance to corrosion and high durability, their only defect being poor light-fastness, which can probably be overcome by hydrogenation of the resins.

The authors of these papers are clearly of the opinion that their resin reacts with drying oil in the varnish cook. They do not, however, specifically claim that their resin is 'oil-reactive'.

A certain group of '100 per cent. phenolics' is, however, so described and the description refers to a vigorous reaction with suitably constituted drying oils occurring at about 450° F. and leading to the elimination of water. These resins are derived from alkylated phenols and are prepared at high formaldehyde/phenol ratios, generally using strong alkali as catalyst.³⁸

The position of 'oil-reactive' resins is still substantially as discussed by the present author in 1939.³⁹ There is little doubt that the reaction exists. It is equally true that the reacting oil is too little considered. While it is true that for a resin to be 'oil-reactive' the phenol/formaldehyde ratio must be of the order of 1:2,⁴⁰ it is equally true that the oil must be of suitable structure and preferably have some degree of conjugation.

The exact nature of the reaction is a matter of controversy. Hilditch⁴¹ regards the action as occurring at double bonds. H. Hönel (who is chiefly responsible for the commercial development of this type of product) regards it as occurring at an 'activated' methylene group lying between two double bonds.⁴² The evidence favours the former view. It should be particularly noted that the reactivity is greatest where there are no 'activated' methylene groups as in tung oil and that it increases as linseed oil is bodied, that is as such groups disappear.

Few workers (except K. Dold⁴³) dispute the existence of the oil-reactivity of this or indeed any type of resin, although they dispute as to the nature of the reaction and the balance of chemical and physical forces involved. The question has recently been discussed by Zeidler and Hesse⁴⁴ from the viewpoint of elongation and other mechanical properties of films from varnishes based on differing types of phenolic resin. It is concluded that certain resins do react with oil.

There has, however, developed a tendency to regard the high formaldehyde alkyl phenol resins as the only reactive resins, whereas in fact they only effect a specialized kind of oil-reactivity. There is a further tendency to regard this special reactivity as a source of excellence, irrespective of other considerations. This view neglects a variety of other factors such as the heat-reactivity of the resin itself, unsaturation of the oil, and the effect of phenols on the bodying of the oil.⁴⁵ In practice no special merit attaches to varnishes based on 'oil-reactive' resins unless they are formulated with all these factors in mind. There is, for instance, no doubt that tung-oil varnishes from 'unreactive' resins are more durable than those from the 'oil-reactive' type. The great advantage of the oil-reactive resins is the light-fastness of the varnishes given by them, and their greater adaptability to long oil varnishes containing linseed oil. This, however, probably has nothing to do with their reactivity, but is more likely to be associated with the alkyl substituent. This invariably contains secondary or tertiary carbon atoms, so that quinonoid changes leading to the development of colour are impossible with this class of material.⁴⁶

There have recently been developed so-called 'heat-hardening' 100 per cent. phenolics (such as Bakelite BR. 3360), which are of especial use in conjugation with ester gum. There is an unfortunate tendency for different workers in this field to have their own interpretations of the term 'heat-hardening',⁴⁷ none of which would be accepted by plastics technologists.

The leading work on varnishes based on 100 per cent. phenolics has been carried out, as has been mentioned earlier, by Turkington and his associates. In 1930 V. Turkington, R. Shuey, and W. H. Butler⁴⁸ showed that these resins conferred beneficial effects on tung-oil varnishes as regards drying time, hardness, durability, and alkali resistance. These authors continued their work in 1931.⁴⁹ In 1938 Turkington, Shuey, and Schechter⁵⁰ studied changes in refractive index, density, and iodine value in phenol-formaldehyde varnishes, and concluded that some kind of (unspecified) oil-resin reaction occurs.

The most valuable published work is undoubtedly the recent paper by R. Shuey.⁵¹ This author points out that drying oils must be suitably heat-treated if the best results are to be obtained with phenolic resins. It is further pointed out that such resins affect the polymerization of oils in diverse ways, so that each system must be considered separately. Thus some phenolic resins polymerize rapidly, but do not affect the polymerization of the oil; unsatisfactory systems may easily result in such cases and such resins are chiefly of use in hardening ester gum. Other resins accelerate the polymerization of the oil (e.g. hydroxy-diphenyl resins). Yet other types retard the polymerization of the oil. The probability of chemical reactions in some cases is deduced from the fact that iodine value may fall without any increase in viscosity or in acetone-insolubility. There is also a discussion of the mechanical properties of films of these varnishes, and their behaviour on oxidation, judged from weight-increase and acid-value studies.

Careful control of driers is necessary with varnishes from 100 per cent. phenolics if skinning is to be avoided. Solvents must also be considered with some care. The 'oil-reactive' type leads to stable varnishes with white spirit; other resins (especially at short oil lengths) need aromatic solvents if synevesis and allied troubles are to be avoided.

In closing this section, reference may be made to a group of phenolic resins probably free from formaldehyde.⁵² The reaction of phenol with terpene hydrochlorides (e.g. from pinene and dipentene) yields resinous bodies (essentially phenylol menthanes) which are oil-soluble and give durable light-fast varnishes. These products are, of course, not 'oil-reactive'.

Resins from Low-temperature Tars.

The low-temperature distillation of coal yields a mixture of phenolic bodies, distinct from that occurring in coal-tar. The development of the low-temperature processes has led naturally to an attempt to use these phenolic bodies as the basis of resins. Most of this work has been carried out by G. T. Morgan and his collaborators⁵³ under the auspices of the Chemistry Research Board (D.S.I.R.). It has been shown that oil-soluble resins can be obtained from this raw material, but they were apparently of poor colour. There is no evidence as to the value of these resins from the standpoint of paint technology, and their future is at present quite uncertain.

Alkyd-phenol-formaldehyde Interpolymers.

This combination has been developed largely in order to impart water-resistance to oil-modified alkyd resins, a property in which they are notably deficient. The interpolymerization leads also to products having high initial rate of film set-up, considerable hardness, and gloss retention. The development of this class of product is largely associated with the firm of Beck, Koller & Co.⁵⁴ Many of these products contain rosin in addition to phenol-formaldehyde resin and drying-oil modified alkyd, but this is not necessarily the case. The methods available for the production of products of this type are very diverse; some of the leading procedures are as follows:

- (1) Phthalic anhydride and glycerol are lightly condensed; fatty acids and rosin, followed by lightly condensed phenol-formaldehyde resin is added.
- (2) Phenol-formaldehyde resin is added to a glycerol-phthalic anhydride-rosin complex, followed by the addition of fatty acids.
- (3) Rosin is combined with lightly condensed phenol-formaldehyde resin, followed by the constituents of the alkyd resin.

It is necessary, for a satisfactory product to be obtained, that tung oil should predominate over linseed oil. Short and medium oil-length products are more common with this class of resin, which is especially suitable for primers, surfacers, &c.

Spirit-soluble Resins.

These products, mentioned earlier, dry by evaporation only. The Novolac type prepared by acidic condensation have been much considered as shellac substitutes.⁵⁵ The scarcity and price fluctuation of shellac in the inter-war years stimulated work on these products, but the stabilization of the shellac position and the rapid progress of research work on shellac has greatly altered this position, and this incentive is largely lost. In any case no true shellac substitute has yet been found. The development of industrial nitrocellulose also militated against the use of these products.

Since 1933 great endeavours have been made to improve and export shellac, this work being largely under the direction of the London Shellac Research Bureau. As a result many improved types of shellac lacquers based on improved forms of shellac are now available. Materials of this type are very fully discussed in the technical papers issued by the above research organization and to which the reader is referred. Attention may be particularly drawn to Technical Paper No. 19 which discusses the combination of shellac and nitrocellulose which may have a very considerable future, and which also contains a complete and valuable bibliography on the industrial applications of shellac lacquers. The successful issue of all this work upon shellac may have the effect of rendering spirit-soluble phenolic resins less and less important as time proceeds.

The alkali-condensed (resole) types still have, however, a use in stoving finishes requiring the greatest possible resistance to corrosion.

Methods for the production of these products (which are simply A-stage resins, either left as dehydrated syrups or thinned with alcohol) can be found elsewhere.

It is possible to induce hardening of such resins by the addition of considerable quantities of acids (or any source of hydrogen ions). This process,⁵⁶ generally called 'cold catalysis', enables very hard finishes to be applied to surfaces such as wood, which cannot be stoved at high temperatures. The method may have some commercial future, but the instability of the catalysed resin is a drawback.

Styrene-phenol Interpolymers.

Styrene and analogous aromatic vinyl hydrocarbons do not yield oil-soluble polymers. It has, however, been observed that interpolymers of styrene with phenols and phenol ethers prepared in the presence of stannic chloride and similar catalysts are oil-soluble.⁵⁷ These polymers are water-white and light-fast. These products may have a considerable future, depending on the industrial development of styrene (already far advanced in Germany) and its cost. The complexes so obtained can be further reacted with aldehydes to give new resins.⁵⁸

Very quick-drying pale light-fast varnishes can be made by the ternary interpolymerization of phenols, styrene, and drying oils, using stannic chloride, and similar catalysts.⁵⁹

These interpolymerizations are probably possible because the catalysts selected promote the formation of polystyrenes of low molecular weight, as has been shown by G. Williams.⁶⁰

Typical Phenolic Varnish Resins

<i>Name</i>	<i>Type</i>	<i>Maker</i>
Lewisol 115, 120, 125, 150, &c.	Modified	J. D. Lewis Inc.
Lewisol 200, 300	100 per cent.	" "
Paradura 367, 10 P, &c.	" "	Paramet. Chem. Corp.
Paranol 105, 200, 500 H, &c.	Modified	" "
Durez 500, 525, 550	100 per cent.	Gen. Plastics Inc.
Superbeckacite 1001	" "	Beck Koller, Ltd.
Superbeckacite 2000	Terpene-phenol	" "
Beckacites 1100, 1101, 1108, 1112	Modified	" "
Beckosols 1320, 1303, 1, 1430	P.F.-alkyd	" "
Beckopol 1400	Fossil-gum P.F.	" "
Bedesol 66	Modified	I.C.I., Ltd.
Bedesol 199	P.F.-alkyd	" "
Bakelite XR. 254, BR. 3360	100 per cent.	Bakelite, Ltd.
Bakelite BR. 2963, 2072	Modified	" "
Bakelite BR. 302, 2175	Oil-modified	" "
Albertol 111 L, 209 L, 326 R	Modified	Albert Products, Ltd.
Albertol 142 R, 237	100 per cent.	" "
Albertol K 6 s	Spirit-soluble	" "
Duropheno 218 v	Oil-modified	" "
Albertalate 222 A	P.F.-alkyd	" "
Phenac 622 N, &c.	Various	American Cyanamide

REFERENCES

1. N. J. L. Megson, *J.S.C.I.*, 1933, 52, 420 T.
2. Mertens, *Mem. inst. color Belge*, 1935.
3. Hellinckx, *Paint Tech.*, 1939, 4, 235, 273, 325, 337, 349, 358, 375; 1940, 5, 11, 49.
4. Boesken, *Rec. trav. chim.*, 1927, 46, 619.
5. J. Schelber, B.P. 306,452; A. V. Blom, *Varnish Making*, p. 25.
6. *Ind. Eng. Chem.*, 1940, 32, 763.
7. *Farben-Ztg.*, 1933, 38, 1018.
8. *J.S.C.I.*, 1934, 53, 1 T, 21 T.
9. *J.C.S.*, 1940, p. 1339.
10. *Farbe u. Lack*, 1929, p. 586.
11. K. Melnel, *Fette u. Seifen*, 1937, 44, 9.
12. T. F. Bradley and W. B. Johnston, *Ind. Eng. Chem.*, 1940, 32, 802.
13. See bibliography to ch. vii. of H. K. Dean, *Utilization of Fats*.
14. *J.S.C.I.*, 1936, 55, 229 T.
15. *Ind. Eng. Chem.*, 1937, 29, 440, 579.
16. *J. Oil Col. Chem. Assoc.*, 1933, 16, 231; 1934, 17, 119; 1936, 19, 42; and cf. Chapter XVI, p. 482.
17. B.P. 1,269.
18. B.P. 15,875; U.S.P. 1,205,081.
19. *Varnish Making*, p. 80.
20. R. L. Houck, *Paint Oil Chem. Rev.*, 1928, 86, 10.
21. Staudermann, *Ind. Eng. Chem.*, 1928, 20, 674; Fonrobert, *Farben-Ztg.*, 1929, 34, 2669; Wolff, *ibid.*, 1927, 32, 2135; 1928, 33, 1724; Barry, *Chem. and Ind.*, 1928, p. 501; 1930, p. 69.
22. Various publications of Albert Products, Ltd.
23. *Ibid.*
24. *Varnish Making*, p. 99.
25. *Ind. Eng. Chem.*, 1932, 24, 871.
26. B.P. 444,853; B., 1936, 216.
27. U.S.P. 2,007,333; B., 1936, 653.
28. U.S.P. 1,212,738, 1,632,113.
29. U.S.P. 1,837,833, 1,677,417; B.P. 267,736, 203,453; B., 1933, 721.
30. B.P. 345,276, 320,313, 345,310, 413,718; B., 1931, 680; B., 1930, 780.
31. *J. Oil Col. Chem. Assoc.*, 1932, 15, 106.

32. *Farben. Chem.*, 1939, 10, 68.
33. U.S.P. 1,959,293; B., 1935, 297.
34. U.S.P. 1,892,990; B., 1934, 254.
35. B.P. 433,539 (Morgan and Drummond); B., 1935, 1005.
36. Author, unpublished observations.
37. *J. Oil Col. Chem. Assoc.*, 1938, 21, 260.
38. B.P. 334,572, 417,122 (Hönel); B., 1930, 1164; B., 1934, 1071.
39. *Varnish Making*, p. 107.
40. Hönel, loc. cit., p. 247.
41. *J.S.C.I.*, 1935, 54, 111 T.
42. B.P. 334,572; B., 1930, 1164.
43. Dissertation, Zürich, 1939.
44. *Fette u. Seifen*, 1940, 47, 146.
45. F. J. Siddle, *Varnish Making*, p. 116
46. B.P. 435,762, 432,796; B., 1935, 1154.
47. Hönel, loc. cit., p. 247.
48. *Ind. Eng. Chem.*, 1930, 22, 1133.
49. *Ibid.*, 1931, 23, 791.
50. *Ibid.*, 1938, 30, 984.
51. *Ibid.*, 1940, 32, 921.
52. Beck, Koller Co., F.P. 792,662.
53. *J.S.C.I.*, 1930, 49, 245 T; 1931, 50, 191 T; 53, 74 T.
54. U.S.P. 1,870,453-4-5, 1,988,354.
55. B.P. 159,494; G.P. 301,374, 304,384, &c.
56. B.P. 471,979, 472,228, B., 1938, 695; B., 1938, 695.
57. I.G. Farbenind., B.P., 489,973, 456,359; B., 1938, 1331; B., 1937, 119.
58. *Ibid.*, B.P. 493,082; B., 1939, 294.
59. B.P. Appn. 10,448/40 (H. S. Lilley).
60. *J.C.S.*, 1940, 746.

CHAPTER X

UREA-FORMALDEHYDE RESINS FOR VARNISHES AND ENAMELS

By J. R. ALEXANDER

It is only comparatively recently that urea-formaldehyde resins have become important raw materials for varnish coatings. In order to produce a resin suitable for coating compositions it was necessary to effect a change in the solubility of the original water-soluble moulding-powder type of resin. The water-soluble resins were replaced by the alcohol-soluble type, which was in turn superseded by the hydrocarbon-soluble resins. One of the latest developments is the petroleum distillate (or white spirit) soluble urea-formaldehyde resin.

The chemistry of the condensation of urea with aqueous formaldehyde in the presence of a monohydric alcohol is dealt with in a paper by H. C. Cheetham.¹ The author considers that mono- and di-methylol compounds are first formed as in aqueous solution, and then the alcohol combines with these to form ether or acetal derivatives, which condense relatively slowly and become more and more soluble in hydrocarbons as the reaction proceeds. T. S. Hodgins and A. G. Hovey² also deal with the mechanism of this condensation. These workers hold the view that the first stage in the reaction is the condensation of formaldehyde with the alcohol to yield a formal (e.g. butyl formal). This formal then reacts with urea to give the so-called condensation unit which may polymerize in a manner similar to dimethylol urea (cf. Chapter IV, p. 176).

Within the last few years a considerable number of patents have been granted for the manufacture of urea-formaldehyde resins for coatings. They may be classified in three main sections:¹ the condensation of urea with aqueous formaldehyde, the water being removed and replaced by organic solvents such as alcohols or hydrocarbons;² the condensation of urea with dry para-formaldehyde in organic solvents;³ the preparation and isolation of solid dimethylol urea and its solution in alcoholic solvents (cf. Chapter IV, pp. 177-80).

The earliest reference to the replacement of water in urea-formaldehyde resins by organic solvents is contained in a patent granted to Fr. Pollak.³ Another example of this method is given by Albert Products, Ltd.,⁴ who describe the condensation of urea with aqueous formaldehyde in the presence of water-insoluble alcohols such as benzyl alcohol. Urea, formalin, and benzyl alcohol are first heated to 90-5° for 30 minutes. The mixture is then acidified with phosphoric acid and heated for a further period of 15 minutes, after which it is cooled and neutralized. The aqueous layer which separates out is removed by centrifuging and a clear benzyl alcoholic lacquer is

obtained which can be air-dried or stoved. Resinous Products Corporation⁵ describe a similar method in which the water introduced by the aqueous formaldehyde is removed by distillation under reduced pressure.

The use of paraformaldehyde in place of aqueous formaldehyde is illustrated by a patent granted to Resinous Products Corporation.⁶ 60 lb. of butanol and 40 lb. of paraformaldehyde are refluxed in the presence of 0.8 lb. of hexamethylene-tetramine until solution is complete; 32 lb. of urea are then added and the mixture is heated gently to 103°, when it begins to boil. After 30 minutes 0.08 lb. of formic acid is added and distillation is begun. Water and butanol distil over, the former being collected and the latter returned to the reaction mixture. Distillation is continued for 12–14 hours, when 1 vol. of the resin solution is miscible with 7–8 vols. of xylol.

S. L. M. Saunders and L. W. Coveney⁷ describe the preparation of a resin soluble in aromatic and aliphatic hydrocarbon solvents from mono- and di-methylol urea and a monohydric alcohol, and Saunders⁸ also uses gelatinized dimethylol urea in butyl alcoholic solution for the preparation of a lacquer resin. A. Hill and E. E. Walker⁹ and I.C.I. describe the preparation of a resin from alkyl carbamates and paraformaldehyde. Other patents deal with the manufacture of lacquer resins from urea and higher aldehydes¹⁰ and also the combination of dimethylol urea and alkyd resins.¹¹ Light-resistant resins with good film-forming properties can be obtained by heating a polyurethane such as di-urethane and ethylene glycol with formaldehyde to 100° according to a patent granted to I.G. Farbenindustrie.¹²

Urea-formaldehyde resins are essentially thermo-hardening resins, and as such their main application has been in stoving industrial finishes. Although these resins can be used alone for colourless, light-fast, and heat-resistant varnishes, they are used chiefly in combination with glycerol-phthalic anhydride (alkyd) resins, usually oil-modified. Urea-formaldehyde resins and alkyd resins are, in fact, complementary, each type imparting to the other a number of most desirable properties.

The advantages of urea-formaldehyde resins in industrial stoving finishes can be stated as follows:

- (1) Being colourless, they improve the colour of the alkyd resin finish in proportion to the amount used.
- (2) Being light-resistant, they reduce the 'after-yellowing' in alkyd varnishes and enamels.
- (3) Being heat-resistant, they reduce the tendency of alkyd resin finishes to yellow on baking at 250–300° F.
- (4) On baking they yield films similar in hardness to vitreous enamel and increase the hardness of alkyd finishes to a remarkable degree.
- (5) This increase in hardness is obtained in a much shorter baking period than is possible with pure alkyd finishes and in many cases at much lower temperatures.

These properties make urea-formaldehyde resins particularly suitable for certain applications. Thus, for example, for refrigerators, hospital equipment, kitchen cabinets, &c., colour retention, hardness, and grease-resistance are of paramount importance. Again, for motor-car steering-wheels, wheel disks, metal furniture, bathroom fittings, hardware, &c., scratch-proofness and resistance to moisture, perspiration, and abrasion are required. Urea-alkyd resin enamels are also resistant to oil, petrol, alcohol, and other solvents, and are therefore extremely suitable for automobile wings, head-lamps, radiators, café table-tops, &c. Gas and electric fires, electric irons, and washing-machines are other applications where the hardness and heat-resistance of these finishes make the replacement of vitreous enamel possible.

With each development in the field of urea-formaldehyde resins the water-resistance has been improved, and it is now possible to add these resins to alkyd stoving finishes, without detracting in any way from the durability of the latter, if a stoving schedule of $\frac{1}{2}$ -1 hour at 250-300° F. is observed.

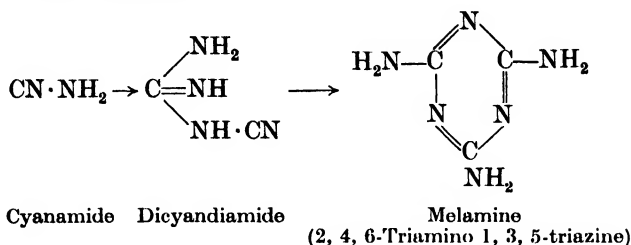
Urea-formaldehyde resins are completely compatible with nitrocellulose, and although urea resin-nitrocellulose combination lacquers have not been used in this country to any great extent, a very large proportion of the urea resins manufactured on the Continent, especially in Germany, is used for nitrocellulose finishes. Unlike the natural resins such as damar, urea-formaldehyde resins are colourless and unaffected by ultra-violet light. They have very low acid numbers, some being neutral. They give extremely hard finishes when combined with nitrocellulose, and such finishes are unaffected by petrol and oil. Urea resin-nitrocellulose lacquers can be rubbed down much more easily than those containing natural resins.

Although, as previously noted, urea-formaldehyde resins belong to the thermo-hardening type, they may be hardened by acid catalysts at ordinary temperatures. This new development described by T. S. Hodgins, A. G. Hovey, and P. J. Ryan,¹³ enables air-drying urea-alkyd resin varnishes and enamels to be formulated without the addition of nitrocellulose, and therefore free from the restrictions and regulations which the latter involves.

Melamine Resins for Coating Compositions.

Melamine-formaldehyde resins are the latest addition to the amino-formaldehyde group. Until recently melamine was a chemical compound of purely academic interest, but it is now manufactured commercially from cyanamide or dicyandiamide by a number of patented processes. The 'di-cy' is usually heated at 120-200° under pressure with liquid ammonia, and this method,¹⁴ which is used on the Continent, is claimed to give a yield of 80-90 per cent. melamine. In this country a process for the manufacture of melamine from dicyandiamide in ordinary plant without the use of pressure has been developed and is now in operation. Patent protection has been

obtained for this invention, which promises to be the most economical process evolved to date.



Melamine dissolves in aqueous formaldehyde to give methylol derivatives similar to dimethylol urea. If the condensation is carried further the products are hydrophobe resins suitable for coating compositions, &c. The Society of Chemical Industry in Basle¹⁵ describes two methods for the manufacture of melamine lacquer resins. In the first place neutral aqueous formaldehyde (8 mols.) and melamine (1 mol.) are heated in a boiling water-bath until the melamine dissolves. After 10 minutes' further heating the solution is cooled and allowed to stand for 2 days. The methylol compound crystallizes out and is washed, dried, and dissolved in butyl alcohol acidified with hydrochloric acid. A clear solution is obtained which yields hard films when heated in a thin layer. The second method describes the condensation of melamine (1 mol.) with alcoholic formaldehyde (5 mols.) acidified with hydrochloric acid. After refluxing for 45 minutes a clear solution is obtained which is suitable for addition to nitrocellulose lacquers. A further patent describes the condensation of melamine with aldehydes other than aliphatic mono-aldehydes.¹⁶ Melamine-benzaldehyde and melamine furfural resins are claimed to be suitable for binding agents for moulded or laminated products and textile coatings.

Melamine-formaldehyde resins for varnishes and other coating compositions are now marketed in America by the American Cyanamid Co. and in Britain by the Beetle Products Company. The most outstanding properties of these new resins, which are also of the thermo-hardening type, would appear to be:

- (1) Their ability to yield extremely hard, glossy films when baked at comparatively low temperatures (190–200° F.).
- (2) Equally hard films are obtained by baking the resins for very short periods (5–15 minutes) at the temperatures usually employed for urea-formaldehyde resins (250–300° F.).
- (3) Their power to impart outstanding resistance to moisture and chemicals to the finishes into which they are blended.

Melamine-formaldehyde resins are more compatible with non-drying-oil and drying-oil modified alkyd resins than the urea type resins. They are colourless and fast to light and exhibit the property of reducing to a marked degree the tendency of alkyd resins to

discolour at high temperatures. Miscibility with turpentine and petroleum hydrocarbons are two other properties which place the melamine resins ahead of the urea type. Ordinary oleo-resinous stoving varnishes as well as drying-oil modified alkyd finishes can be greatly improved in hardness and water-resistance by the addition of small percentages of melamine-formaldehyde resins.

Like the urea resins the melamine resins are compatible with nitro-cellulose, and such combination finishes are extremely hard and glossy.

Water-soluble Resins.

A number of water-soluble resins are mentioned in a paper by L. Light,¹⁷ but the most important are the urea-formaldehyde resins for textile coating. Innumerable patents have been taken out in this country and in America for different textile processes, using urea-formaldehyde resins, and new patents are still being granted. The advantages of such processes are shown in the crease-resistance, strength, flexibility, and resistance to washing of the treated fabrics. Increased affinity for dyes and fastness to light are other properties imparted to textiles treated with urea-formaldehyde resins.

It is noteworthy that a number of new patents on textile treatment claim melamine-formaldehyde resins as suitable agents.

A recent patent¹⁸ granted to Sir Thomas and Arthur Wardle, Ltd. describes the treatment of viscose fabric with an aqueous urea-formaldehyde condensation product and a water-soluble inorganic ester, such as glycerine triborate; such treatment is claimed to give increased resistance to creasing and an increase in wet tenacity.

Tootal, Broadhurst Lee Co., Ltd. claim a process for de-lustring non-crush textiles. 120 gm. of urea and 150 c.c. of 40 per cent. formaldehyde (neutral) are allowed to stand for some hours at room temperature. The textile is impregnated in a 50 per cent. aqueous solution of the condensation product, excess liquor removed, and then dipped in 4 per cent. HCl solution until de-lustring has taken place. The material is then washed, dried, and impregnated again, in 20–40 per cent. formaldehyde solution acidified with 0.75 per cent. tartaric acid. After squeezing and drying, it is heated for 2 minutes at 170°.¹⁹

The chief advantages obtained by the use of melamine-formaldehyde resins in textile-treating lies in the fact that the fabric can be dried at a much lower temperature than that necessary when urea-formaldehyde (or phenol-formaldehyde) resins are employed.

Society of Chemical Industry in Basle²⁰ describes a process in which cotton satin is impregnated with an aqueous solution of melamine-formaldehyde resin using formic acid as the catalyst. After squeezing, the fabric is dried at 50–60° instead of at 140–150°, which is the general drying temperature for urea-formaldehyde impregnated fabrics. It is claimed that the dressing on such a fabric is unaffected by washing for $\frac{1}{2}$ hour at 90° in a 0.5 per cent. soap solution. A further patent²¹ claims an improvement in the resistance to washing of

starch-dressing in cotton fabrics by the addition of a melamine-formaldehyde syrup.

By rigid control of the pH during condensation it is possible to obtain water-soluble phenol-formaldehyde resins which are suitable for textile impregnation.

Water-soluble vinyl ketone-aldehyde resins and vinyl acetal resins have also been prepared. Suggested uses are in adhesives and light filters. Vinyl ether resins, such as polyvinyl methyl ether, combine water-solubility and adhesive power.

Glycol maleate resins and glycerol citric acid resins can be made water-soluble, the latter resembling in some respects the glycol borate type of resin.

It is noteworthy that although the new polyamide resins such as the Nylon resins are insoluble in water, it is possible to obtain water-soluble resins of very similar constitution. Thus E. I. du Pont de Nemours²² claim that the resin from adipic acid and triglycol-diamine is soluble in water and the I.G. Farbenindustrie²³ state that water-soluble resins are obtained from maleic anhydride, ethylene diamine, and formaldehyde. Fabrics spun from these water-soluble resins are useful as ground fabrics in embroidery manufacture.

Among the water-soluble ketone-formaldehyde condensation products Zwicky, Brunner, and Cilander A.-G.,²⁴ claim that the resin obtained from the alkaline treatment of acetone with formaldehyde yields on impregnation shrink-resisting fabrics. The resin from methyl ethyl ketone can also be obtained as a glass-clear water-soluble syrup.²⁵

Acrylic resin emulsions (e.g. the Plextols) are now available to the textile trade. One of the most recent of these vinyl compounds is the co-polymer of methyl methacrylate and 2-ethyl-hexyl acrylate described by A. Renfrew, W. E. F. Gates, and I.C.I., Ltd.²⁶ These resins impart outstanding water-resistance and flexibility to fabrics.

REFERENCES

1. H. C. Cheetham, *Official Digest*, 9, No. 174 (1938).
2. T. S. Hodgins and A. G. Hovey, *Ind. Eng. Chem.*, 1938, 30, 1021.
3. B.P. 238,904; B., 1925, 891.
4. B.P. 517,196; B., 1940, 296.
5. B.P. 511,087; B., 1940, 153.
6. B.P. 498,043; B., 1939, 633.
7. B.P. 484,200; B., 1938, 943.
8. B.P. 501,388; B., 1939, 749.
9. B.P. 491,857; B., 1939, 294.
10. B.P. 494,700; B., 1939, 405.
11. B.P. 344,401; B., 1931, 597.
12. B.P. 491,499; B., 1939, 294.
13. *Ind. Eng. Chem.*, 1940, 32, 334.
14. B.P. 466,957; B., 1937, 762; B.P. 502,148; B., 1939, 580; B.P. 513,760; B., 1940, 34.
15. B.P. 466,096; B., 1937, 1376.
16. B.P. 468,746; B., 1937, 1089.
17. *Chemical Age*, 1940, 333.
18. B.P. 501,206; B., 1939, 714.
19. B.P. 499,207; B., 1939, 597; B.P. 467,480; B., 1937, 1332.
20. B.P. 477,841; B., 1938, 266.
21. B.P. 466,015; B., 1937, 755.
22. U.S.P. 2,191,556.
23. F.P. 849,848.
24. U.S.P. 2,159,875
25. *Rr. Plastics*, June 1939, 35
26. B.P. 503,140; B., 1939, 714.

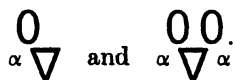
CHAPTER XI
ALKYD RESINS

By E. A. BEVAN

INTRODUCTION

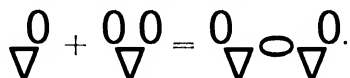
THE alkyd resins, sometimes known as 'glyptals', are formed by the condensation of polybasic acids with polyhydric alcohols, the typical member of the group being that formed by condensation of phthalic anhydride with glycerol.

The chemistry of the process has been outlined in the introductory chapter, and will be discussed in further detail in the chapter on the problems of resinification. Nevertheless it may be of advantage to refer briefly here to the opinions of some investigators. In the first published study of kinetic data of the glycerol-phthalic anhydride reaction, R. H. Kienle and A. G. Hovey¹ concluded that the process proceeds by esterification only in a gradual and continuous manner, yielding a heterogeneous complexity of esters and finally the formation of more complex structures. Gelation occurs regardless of temperature at an esterification value of 75-79 per cent., that is to say, before esterification is able to complete itself. Doubt is expressed that the esterification takes place in steps such as the formation of a monoglyceride, then a diglyceride and finally a triglyceride, and no confirmation could be obtained of the intermediate formation of acrolein as suggested by Drummond and Morrell.² This study was extended to the reaction of ethylene glycol and phthalic anhydride,³ which had already been described by Kienle and Ferguson⁴ as a reaction belonging to the heat non-convertible type. Again it was concluded that esterification was the only reaction occurring, which took place according to the chance meeting of the individual alcohol and acid radicals resulting in a mixture of esters instead of the formation of simple mono- and di-esters. The reaction differs from the glycerol phthalate reaction in that gelation does not take place at any temperature and esterification can be carried out practically to completion. Hönel⁵ found that equivalent amounts of glycerol and phthalic anhydride very quickly react to yield a product with an acid number of 267, which would indicate a mixture of the monobasic monoglyceride with the dibasic diglyceride, which may be represented by symbols as follows, where \bigcirc indicates a dibasic acid and ∇ a trihydric alcohol:



The constant of the reaction shows a marked change when about one-

third of the COOH groups have been esterified, which may indicate that the reaction has reacted as follows:



(In this case the equilateral triangles signify that both α and β OH groups of the glycerol enter the reaction.) This latter compound may condense further to form chain-like formations and even ring structures. He considered that at the gel stage a diverse mixture of different-sized molecules up to very large ones with acid properties are present together with not more than a very small quantity of completely esterified product. Only the larger molecules possess colloidal properties which, however, may be so pronounced that gelation might occur with a relatively high proportion of lower-stage condensation products present. Progressive esterification is the cause of the transition to the gel stage and this progresses even farther on continued heat treatment.

G. Bozza⁶ states that the lower reactivity of the secondary hydroxyl leads to the formation of molecules having lower saponification values and that a 50 per cent. esterification stage is rapidly reached, the products having low molecular weights. A second stage again produced by esterification is reached more slowly when both α -hydroxyl groups of the glycerol are neutralized at a molecular weight of 610. This corresponds with Hönel's formula given above:



but differs in that Bozza considers that only the α -hydroxyls of the glycerol are esterified. W. E. Wornum⁷ states that at higher temperatures the secondary or β -hydroxyl becomes more active, but R. Houwink⁸ is against this view. In the third or gelation stage Bozza (loc. cit.) differs again from Hönel and considers that the molecular weight increases without increase in the degree of esterification, by anhydride formation between free acidic groups of two adjacent molecules, more water being eliminated.

The glycerol-phthalate reaction has been reinvestigated more recently by R. H. Kienle, P. A. van der Meulen, and F. E. Petke⁹ under strictly controlled and reproducible conditions at temperatures ranging from 160 to 215°. When equivalent quantities of glycerol and phthalic anhydride are employed, they showed that the amount of water evolved was less in the early stages and greater in the later stages than that calculated from simple inter-esterification considerations, which indicated that both anhydride formation and intra-esterification were definite possibilities, there being no evidence whatsoever of any ether formation. On this basis it has been possible to derive certain approximate compositions of glyceryl phthalate polymericides at various stages of condensation, which tend to fall into

groups of type species rather than varying continuously. Thus it is concluded that three-dimensional polyester molecules are not formed until an acid value of approximately 137 is reached. The earlier idea that the reaction proceeds entirely in a heterogeneous manner by random chance contact of the active groups of the interacting molecules is therefore now questioned (cf. Chapter XVI, p. 477).

Gelation apparently may occur when there is formed a sufficient concentration of suitably complex three-dimensional polymers of relatively low molecular weight which are capable of intertwining and bringing about a state of arrested motion and is not necessarily due to the formation of large macromolecules.

The technical development of these resins on a commercial scale depended largely upon the production of phthalic anhydride in large quantities at a comparatively cheap rate by the catalytic process developed by C. R. Downs¹⁰ and H. D. Gibbs and his collaborators.¹¹ Other dibasic acids such as succinic and adipic acids* are used to a slight extent, and maleic acid owing to the properties conveyed by its conjugated double linkage to an increasing extent. Glycerol and to a very much less extent ethylene glycol are still practically the only polyhydric alcohols employed, although the commercial production of sorbitol and mannitol opens up new possibilities.

The commercial production of alkyd resins has expanded at a very rapid rate during the last ten years, being used principally in paints, varnishes, and lacquers. The condensation product is almost always modified to give particular properties for each specific application, the modifying agent usually being a fatty acid derived from a non-drying, semi-drying, or drying oil or natural resin. The unmodified alkyd resins have not yet become commercially important. The table below¹² illustrates the rapid increase in production in the United States for the period 1933-7, during which time the number of manufacturers of this type of resin increased from 6 in 1933 to 39 in 1937.

Year	No. of makers	Production pounds	Quantity	Sales	
				Value	Unit value
				\$	\$
1933	6	9,930,705	3,654,854	673,890	0.18
1934	10	15,219,247	7,084,602	1,022,436	0.14
1935	15	34,312,713	15,836,942	3,482,078	0.22
1936†	31	46,952,452	24,252,535	5,312,121	0.22
1937†	39	61,254,019	34,738,295	6,864,194	0.20

† Includes resins from maleic anhydride.

The opinion is expressed that the volume of production of resins from maleic anhydride will in the near future approach that from phthalic anhydride.

* Adipic acid ($C_6H_{10}O_4$) can be obtained in 50 per cent. yield by oxidation of cyclohexane by air at 94-120° in the presence of cobalt chloride as catalyst (du Pont de Nemours & Co., U.S.P. 2,223,493).

HISTORICAL

The development of the polyhydric alcohol-polybasic acid reaction from its first discovery to the present-day commercial production may be conveniently divided into four periods, between each stage of which some lapse of time took place.

First Period.

The production of resinous substances by the combination of polybasic acids with polyhydric alcohols was first noted by Berzelius, who obtained a deliquescent solid by heating tartaric acid with glycerol at 150°. He does not, however, appear to have pursued the matter further, and van Bemmelen¹³ was the first to make a more or less detailed study of the reaction. Van Bemmelen experimented with both succinic and citric acids and with different proportions of acid and glycerol. In each case he obtained similar results: a thick syrup on heating at about 160° which, when further heated at about 210°, was finally converted into a hard solid unaffected by water. Similar experiments were carried out by Lourenço¹⁴ using citric acid.

Nothing further of interest seems to have been done until 1901, when Watson Smith¹⁵ studied the case of phthalic anhydride. He heated a mixture equivalent to diglyceryl triphthalate, distilling off the excess glycerine *in vacuo*. He noted that the conversion to a hard water-insoluble substance occurred at about 200-10° and was a strongly exothermic reaction. As the same ultimate product was obtained with varying proportions of the reagents, Watson Smith concluded that the product was a glyceride of phthalic acid, and he made the prophetic suggestion that it might be used as a cement.

Little seems to have been done to apply these isolated results to industry or to study the phenomena more deeply from the purely scientific point of view.

Second Period.

The second period may be said to begin with a long series of patents taken out mainly by the General Electric Company and the Barrett Company of the United States of America in 1913 and subsequent years, and by the British Thomson-Houston Company in this country.

This burst of activity was, as already mentioned, due to the appearance of a cheap and abundant supply of phthalic anhydride. As the catalytic process also provided maleic, malic, succinic, fumaric, and benzoic acids, the possibility of commercial development of the glyptal type of resin was assured at least from the economic point of view.

Although the number of patents is large and the modifications suggested numerous, there is little of scientific interest in them, and they may not unfairly be summarized as merely more or less detailed descriptions of the means of transferring to a factory scale the

laboratory processes already described by the workers of the first period, with more or less important modifications in the matter of heat treatment, and the use of the various alcohols and acids either already described by earlier workers or closely related to them chemically.

In a British Thomson-Houston patent¹⁶ phthalic anhydride is heated with an equal weight of glycerol to 185° until a drop of the mixture solidifies on cooling. This substance is soluble in acetone. On raising the temperature to 210° a vigorous reaction occurs after some time with the evolution of heat, and the product becomes insoluble in acetone. If the temperature be raised to 275° the reaction is very violent. In either case, the violence of the reaction is sufficient to produce bubbles in the heated mass, and in order to avoid this M. Callahan¹⁷ proposed the use of lower temperatures (85–130°) for longer periods, followed by heating at 183° and finally at 250°.

The use of acids other than phthalic is referred to in a patent of the same year.¹⁸ The use of castor oil as a plasticizer is the most interesting feature of this patent.

W. C. Arsem of the General Electric Company¹⁹ developed the idea of using fatty substances, replacing part of the phthalic acid by its molecular equivalent of oleic acid; 92 parts of glycerol were heated with 148 parts of phthalic anhydride to 210°, and the mixture of 141 parts of oleic acid and 37 parts of phthalic anhydride added. The temperature was then again raised to 210°. After about 1½ hours a thick reddish mass was obtained which was soluble in acetone, but became insoluble on heating at 160° for from 20 to 30 hours. Increase of the oleic acid content increased the flexibility. In the corresponding English patent²⁰ covering much the same ground the use of castor oil in place of oleic acid is described, whilst lactic and palmitic acids are also mentioned as replacing part of the phthalic acid.

Succinic acid, which had been used by van Bemmelen, is referred to in a patent granted to the British Thomson-Houston Company,²¹ but it is pointed out that the nature of the product is dependent on the way in which the succinic acid is introduced. Equimolecular proportions of phthalic anhydride and glycerol are heated and then combined with ½-molecular proportion of succinic acid by heating at 210–25°. A plastic mass is obtained which, however, loses its plasticity on prolonged heating at 200°. A soft product can be obtained by replacing the succinic acid by stearic acid. With lactic acid and with monochloroacetic acid a range of products of varying degrees of hardness and plasticity can be obtained according to the proportion used and the time and temperature of heating.

A comprehensive patent by M. Callahan²² includes malic acid as increasing the plasticity of the product, and states that glycerol can be replaced by mannitol. Callahan also paid considerable attention to the question of temperature and duration of heating, and noted that the time required for conversion of the soluble to the insoluble form was dependent upon the mass of the material. Thus 75 gm. of a succinic-citric-acid resin was converted to the insoluble

form in 15 to 20 minutes at 160°, whilst 900 gm. required 3 hours for conversion at the same temperature.

With the patenting of the use of camphoric acid²² and butyric acid²³ the list of acids and bases commercially usable may be said to be completed.

The use of additional substances as plasticizers received a certain amount of attention. The introduction of sulphur²⁴ to produce a rubber-like substance is of interest. The procedure suggested is as follows:

Ninety-two parts of phthalic anhydride are heated with 148 parts of glycerol at 200° until frothing ceases; 282 parts of oleic acid are then added, the temperature being kept below 232°. From 10 to 30 parts of fine sulphur are added. Greater flexibility can be obtained by incorporating other substances such as nitrobenzene or ethyl benzoate²⁵ or naphthalene.²⁶ It will be observed that all the patents referred to above were issued in the year immediately preceding the Great War and represent the results of intensive research by the two great electrical firms—the British Thomson-Houston Company of England and the General Electric Company of America. The patents show that the technical possibilities of the fundamental reaction had been fairly thoroughly explored, but left the underlying scientific principles practically unconsidered.

As to practical application, the obvious use of the resins as stoving varnishes and impregnating materials is constantly referred to. The soluble form of the resin is dissolved in a suitable solvent (invariably acetone) and applied to the material in question, which is then baked at a temperature sufficient to convert the soluble resin to the insoluble form. The high electrical insulating properties of such a product is noted, but the comparatively slow transformation to the insoluble form was a disadvantage.

During the Great War work on this subject seems to have been almost entirely suspended, and it was not until 1922 that publication of results recommenced.

Third Period.

A patent by Louis Weisburg of the Barrett Company²⁷ is of importance as defining the stages of the resinification process. Weisburg divides it into three:

A Form. Fusible, soluble in acetone, affected by water.

B Form. Fusible, but insoluble in acetone, though affected by water.

C Form. Infusible, insoluble in acetone, unaffected by water.

Weisburg's classification has been generally adopted with beneficial results to the clarity of subsequent literature.

In a further patent²⁸ the study is extended to the case of the condensation of glycerol with dibasic aliphatic acids. With malic acid it is stated that the *B* form can be converted to the *C* form by immersion in distilled water for 2 minutes. The rate of conversion of the

B form to the *C* form is of great commercial importance, for the output of a moulding plant is determined by the time the mould is occupied by each batch of material.

The slow rate of conversion of the glyptal resins to the *C* form was therefore a serious matter. Louis Weisburg and R. S. Potter²⁹ found that the reaction could be accelerated by first partially polymerizing the glycerol. This is effected by the addition of sodium acetate or sodium hydroxide. The patentees state that by using phthalic anhydride and polymerized glycerol the time of formation of the *A* form is reduced to $\frac{1}{5}$ that required when using unpolymerized glycerol, and the transformation of the *A* form to the *B* form and the *B* form to the *C* form is twice as rapid.

Other catalysts were suggested by J. G. E. Wright,³⁰ who used the oxides of calcium, magnesium, and zinc, and also iron, obtained by reducing the oxide with hydrogen.

C. F. Peterson³¹ made the interesting observation that the addition of small quantities of a phenol-formaldehyde resin accelerated the hardening.

An important innovation in the method of manufacture was made by J. G. E. Wright and W. J. Bartlett,³² who effected the transformation of the *A* form to the *B* form by dissolving it in a solvent, such as diethyl-phthalate (b.p. 292°), the boiling-point of which was high enough to enable the temperature to be raised to a point sufficient to complete the conversion in reasonable time. The transformation can be stopped at any desired stage by precipitating the resin. Using diethyl-phthalate, for example, the reaction mixture is poured into benzene, when the resin is precipitated as a white curd which can be powdered and is rapidly converted to the *C* form.

A further important feature of this method is that it lends itself to the incorporation of oils, such as linseed and China wood-oil, which has proved of considerable importance in the subsequent development of synthetic varnishes.³³

China wood-oil dissolved in diethyl-phthalate together with the glyptal constituents commences to thicken at 100° and is completely dispersed at 200°. On removal of the solvent a viscous mass is obtained which is soluble in aromatic hydrocarbons and gives a tough film on drying.³⁴ M. M. Brubaker claims the use of β -elaeostearin.

The combination of the glyptal condensation products with vegetable oils presents some difficulty. It was, however, the successful solution of this problem which led to the rapid commercial development of this class of resins in the paint and varnish industry, and marks the outstanding achievement of this third period. Arsem had already shown (loc. cit.) as early as 1914 that a portion of the phthalic acid might be replaced by a fatty acid which led to the production of more flexible condensation products, but it was not until 1928 that the logical step of employing an unsaturated fatty acid in place of a saturated fatty acid was found to yield a product with air-drying properties. R. H. Kienle³⁴ heated phthalic anhydride and glycerol

together until an intermediate stage was formed when one or more fatty acids derived from a drying-oil such as China wood-oil, linseed, or perilla were added to the mixture with a further amount of phthalic anhydride, and the heating continued. Alternatively, the phthalic anhydride and fatty acids could be melted together and the glycerol added subsequently. The resins which were obtained were soluble in acetone alcohol-benzene mixtures, coal-tar hydrocarbons, esters, and also in drying-oils such as linseed, China wood, and perilla. Upon air-drying they became hard, insoluble, and infusible. This process came to be known commonly by the term 'Fatty Acid Process' in distinction to other processes later developed. The necessity of first splitting a drying-oil into its components, i.e. free fatty acid and glycerol, before incorporation with a glycerol-phthalic acid resin could be effected, was disadvantageous and further efforts were directed to the incorporation of the free drying-oil itself. This resulted in the development of a number of additional processes.

One of these processes, known as the 'Fatty Acid-Fatty Oil Process', developed by E. E. Walker and R. Hill and Imperial Chemical Industries, Ltd.³⁵ in 1930, may be regarded as an intermediate stage between the true Fatty Acid Process and true Fatty Oil Process. Thus resins are produced by condensing the polyhydric alcohol and polybasic acid in the presence of a monocarboxylic acid, a drying oil being incorporated either before or during the condensation. As an example of this procedure, the following may be quoted:

Thirty-seven parts of glycerol and 74 parts of phthalic anhydride are heated to 200-10° with 50 parts of oleic acid. Ten parts of linseed oil are then added with stirring, and heating is continued until the mixture clears. Four lots of 10 parts of oil are then added in a similar way, heating until clearance between each addition. The temperature is then raised to 220-30° for 2½ hours. The product is a hard, clear, flexible resin, which is soluble in hydrocarbon solvents.

By using different acids a wide range of products can be obtained: thus butyric acid gives a moderately hard flexible resin, whilst stearic acid gives a softer product. In general, monobasic acids of high molecular weight require a greater proportion of oil than do those of lower molecular weight, whilst unsaturated acids, such as oleic acid, yield tougher products than do saturated acids such as stearic acid. The free fatty acids of linseed oil can be used with advantage in conjunction with China wood-oil.

Several processes have been described in which a drying oil may be incorporated directly into the alkyd condensation. One means of effecting this was discovered by Dawson in 1937³⁶ by first preparing a solution of the drying-oil in phthalic anhydride and subsequently heating the solution to a sufficiently high temperature with glycerol.

This process was developed further by P. F. Schlingmann³⁷ so that any proportions of an oil glyceride could be incorporated provided the polybasic organic acid was in chemical excess, this excess being in turn reacted with a polyhydric alcohol to produce a mixed ester resin containing no free oil present. The procedure employed

was to add the oil very slowly to the phthalic anhydride heated to 270–300° under such conditions that a trace of water is continuously kept in the system. Owing to the small amount of water which is always present in a drying oil, there is an equilibrium condition which may be expressed as follows:



Under normal conditions the amount of glycerol and free oil acids are small, but in the presence of a polybasic organic acid the equilibrium is shifted towards the right-hand side of the equation by the removal of the glycerine by the polybasic acid to form a resin. The water thus formed in this condensation reaction is thus available to hydrolyse more fatty oil to yield more glycerine and fatty acids. Provided then that the small amount of water is retained in the system, the oil is continuously hydrolysed to free fatty acids. Thus this process may be considered to be a modification of the 'Fatty Acid Process'.

Imperial Chemical Industries, Ltd., and W. Baird developed a two-stage process whereby a non-hydroxylated fatty oil was incorporated with a polyhydric alcohol and a polybasic acid by heating in an autoclave under elevated pressure, until the mixture became homogeneous, and subsequently completing the reaction in an open vessel.

The 'alcoholysis' or monoglyceride process described by the I.G.³⁹ consists in first forming a partial ester of a polyhydric alcohol and a monobasic acid and subsequently completing the esterification with a polybasic acid. The partial esters or monoglycerides may be formed from a drying oil fatty acid or directly from the fatty oil itself by alcoholysis. Akin to this process is a three-step process described by W. Baird, R. Hill, and Imperial Chemical Industries, Ltd.,⁴⁰ which consists in first condensing a polybasic acid with an excess of polyhydric alcohol, so that free hydroxyl groups are present to the extent of at least one-third of those present in the original polyhydric alcohol, then reacting the product with a fatty oil and subsequently condensing with a polybasic acid to esterify the free hydroxyl groups.

Finally, there are what may be termed the 'Solvent Processes', which consist in using a high-boiling solvent as a flux to enable the dispersion of the oil in the resin to take place. As early as 1924 L. V. Adams and the British Thomson-Houston Co., Ltd.⁴¹ described a process by which a phthalic glyceride was incorporated with China wood-oil by heating in the presence of a high-boiling solvent such as benzyl benzoate which brought about dispersion of the two materials. Incidentally, this process is the first mention of a drying-oil alkyd combination. Imperial Chemical Industries, Ltd., H. H. Morgan, A. A. Drummond, and G. C. Attfield⁴² employed an aliphatic alcohol of boiling-point not above 175° with or without the addition of a hydrocarbon or ester solvent, and reacting all the ingredients together under heat. In this case the aliphatic alcohol is stated to take part in the reaction. The I.G. Solvent Process⁴³ employs a practically inert and water-insoluble solvent having a boiling-point below 200°, which is capable of forming pseudo-azeotropic mixtures with water

vapour, and heating in such a manner that a mixture of the water formed and solvent are continuously distilled off. In one example glycerol, phthalic anhydride, and linseed oil are condensed together in the presence of xylene.

The third period may be considered as complete with the establishment of three fundamental processes for the preparation of drying-oil modified alkyd resins: the Fatty Acid process with which is included the Fatty Acid-Fatty Oil process; the Fatty Oil or Mono-glyceride process; the Solvent or Solution process. All other processes may be related more or less closely to these three fundamental ones.

Fourth Period.

Although the dividing line between the third and fourth periods is not so distinct as between the other periods from the point of view of lapse of time, nevertheless it does mark a new stage in the development of the drying oil-modified alkyd.

This period concerns itself with a more thorough investigation and understanding of the three fundamental processes developed in the previous period. Apart from the claims made for particular modifications, such as the incorporation of phenol-formaldehyde resins, particular drying-oils or their fatty acids and different polybasic acids and polyhydric alcohols to yield specific properties, which are discussed later in this chapter, it has been found necessary to limit to some extent the wide claims already made in regard to the manufacturing processes themselves.

In particular is this true in regard to the use of maleic acid or anhydride to replace phthalic anhydride in the Fatty Acid Process. In the various patents for the basic processes already described, it has been generally and sometimes particularly claimed, that such processes are equally applicable to the use of other polybasic acids such as succinic, malic, maleic, fumaric, tartaric acids, &c. In actual fact phthalic anhydride cannot always be replaced by a water-soluble aliphatic polybasic acid in such compositions and often leads to the formation of two immiscible layers instead of a uniform resinous product, unless strictly limited proportions or other conditions are employed.

S. L. M. Saunders⁴⁴ considers the governing factor in producing homogeneous reaction products from different polybasic acids to be (1) whether the ester formed between the acid and polyhydric alcohol is, at least in its initial stages, soluble in water or not, and (2) only when water-insoluble esters are obtained as in the case of phthalic and adipic acids will homogeneous products be obtained without difficulty. The solubility of their primary esters with polyhydric alcohols runs parallel with the solubility in water of the acids themselves. One method described by D. G. Anderson and R. L. Yeates⁴⁵ to overcome this difficulty of non-homogeneity is to carry out the condensation of the unsaturated fatty acid, maleic anhydride, and

glycerol in the presence of cyclohexanol or alkyl-cyclohexanol, in which the cyclohexanol acts not only as a flux but combines substantially with the other ingredients.

In a series of patents I. Rosenblum describes the preparation of homogeneous long-oil resins, which are soluble in oil and compatible with varnishes. Whereas the simultaneous reaction of an unsaturated fatty oil acid, glycerol, and maleic anhydride yields non-homogeneous reaction products, by first preparing a partial ester of the fatty oil acid with glycerol homogeneous resins may be obtained with an aliphatic polybasic acid.⁴⁶ Homogeneous long-oil resins may be obtained by carrying out the simultaneous reaction of maleic anhydride, glycerol, and fatty oil acids (in the proportion of at least 1 molecule for each molecule of glycerine) in the presence of a volatile saturated aliphatic acid having up to 5 carbon atoms, for example, acetic acid, or alternatively the acetic acid may first be reacted with the glycerol to form a partial ester.⁴⁷

Mixed polymeric esters of a water-soluble acid and a water-insoluble acid are easier to prepare than those derived from the straight water-soluble acid. The proportion of water-insoluble acid to water-soluble acid necessary to obtain homogeneity, however, depends upon the proportion of fatty oil acids present, and generally speaking the amount of water-soluble acid may be increased as the fatty oil acids ingredient decreases. In the preparation of long-oil resins which are themselves soluble in oils, I. Rosenblum employs a mixture of phthalic and maleic acids in which the quantity of the latter does not exceed 15 per cent. by weight of the phthalic acid, and the condensation is carried out by the simultaneous reaction of the polybasic acid mixture, the fatty oil acids and glycerol.⁴⁸ The amount of fatty oil acids necessary in such a composition to yield oil-solubility would be about 40 per cent., but it was found that by increasing this proportion to unusually high amounts, so that they are in excess of 1 molecule for each molecule of total dibasic acid (i.e. of the order of 65-75 per cent.), then the proportion of maleic acid to phthalic acid could be increased to as high as equimolecular proportions.⁴⁹

For the production of short-oil resins, S. L. M. Saunders proposes that the unsaturated fatty acid is first reacted with a polyhydric alcohol in an amount in excess of 1 molecule to 1 molecule of fatty acid, and just sufficient of a water-insoluble polybasic acid is added (e.g. phthalic anhydride) to form a homogeneous solution, but insufficient to esterify completely all the free hydroxyl groups present, and thereafter the homogeneous solution is heated with maleic anhydride.⁵⁰ Maleic anhydride differs from other polybasic acids previously investigated in the alkyd condensation in possessing an α - β -enal grouping which is capable of reacting with a conjugated double bond according to the Diene synthesis.⁵¹

The commercial production of maleic anhydride and its replacement of phthalic anhydride in alkyd resin manufacture led to the rapid development of new types of ester resins.

One of the very first alkyd resins to be commercially developed

was a glyceryl phthalate condensation modified with a natural resin acid, e.g. rosin or copal. Carleton Ellis⁵² describes the preparation of such a product: 50 parts of phthalic anhydride are heated to 250° with 33 parts of glycerol and 75 parts of rosin. To the clear product of acid value 68 a further 10 parts of glycerol are added and the temperature raised to 290°, when a clear transparent resin is obtained of acid value 12.7 and of somewhat darker colour than the original rosin. Similar products were produced⁵³ either by reacting together a pre-formed glyceryl phthalate resin and a rosin ester at 200–290°, or by reacting one of these compounds with the ingredients of the other. These products possessed very similar physical properties to those of natural resins, but differed considerably in chemical properties. An important property which they did possess was their compatibility in all proportions with nitrocellulose, and the Ellis-Foster Company⁵⁴ claim the manufacture of a cellulose ester composition in which such a resin is incorporated in an amount which exceeds that of the cellulose ester. K. M. Weber⁵⁵ states that it is advantageous to employ condensation products of acid value below 20 and having no free glycerol in order to obtain films which show no tendency to 'blushing'.

When phthalic anhydride is replaced by maleic anhydride in the production of such products considerable improvement in their properties results, not only from the point of view of their use in nitrocellulose lacquers, but also in oil-varnish manufacture, and very rapid commercial development has ensued, which has almost, if not entirely, displaced the earlier phthalic-rosin condensation products. Even before the disclosure of the Diene synthesis, the preparation of a resin by reacting together rosin, maleic anhydride, and glycerol was described by Carleton Ellis⁵⁶ and their application particularly claimed in the manufacture of nitrocellulose lacquers. After the mechanism of the Diels-Alder reaction had been made known, more attention was paid to the use of maleic anhydride in such processes and a conjugated structure was attributed to abietic acid and even to rosin itself, from which it may be produced by the action of heat and acids.^{57, 58} E. A. Bevan casts some doubt on whether the mechanism of the reaction is necessarily one of the Diene synthesis⁵⁹ and shows that the maleic anhydride value of rosin differs quite appreciably according to its source and in all cases is very much below the theoretical value calculated for that of abietic acid.

That the reaction is fundamentally different to that using phthalic anhydride involving more than inter-esterification is made clear from the processes disclosed in the patent literature. The I.G.⁶⁰ first react maleic anhydride with rosin or ester gum at temperatures between 110 and 200° and subsequently esterify the product with glycerol. If sufficient maleic anhydride is employed, the resulting resin no longer exhibits the Storch-Morawski test. Carleton Ellis⁶¹ illustrates the different reactions of phthalic anhydride and maleic anhydride by saponification of the condensation products. In the former case rosin acids are obtained unchanged, whereas in the latter case an acid

compound of rosin is obtained. This compound differs from ordinary rosin acids in having a higher softening-point and higher acid value, and forming solutions in aqueous alkali which are not soapy—like similar solutions of rosin. He concludes that the reaction between maleic anhydride and rosin is that of the Diene synthesis. Apparently, to obtain such products it is not necessary to react the maleic anhydride and rosin together first, since combination between the unsaturated centres of maleic anhydride and rosin may take place by the simultaneous reaction of the glycerol, maleic anhydride, and rosin or by the action of maleic anhydride or a pre-formed ester of rosin.

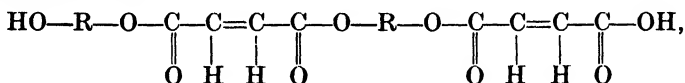
Whereas the application of the phthalic rosin esters was limited almost entirely to their use in nitrocellulose lacquers such as sanding sealers and wood finishes, in which the maleic-rosin esters have now very largely displaced them, the latter have found an increasing application not only in other types of nitrocellulose lacquers but also in the manufacture of oil varnishes, where they are replacing to some extent resins of the reduced phenolic type, particularly for short-oil varnishes where light-fastness is an important characteristic. The maleic-rosin-ester possesses a much higher degree of complexity with a correspondingly higher melting-point than the phthalic-rosin-ester containing the same percentage of rosin; with decreasing percentage of rosin in the condensation product the oil-solubility is impaired, and although it is possible to obtain oil-soluble products from phthalic-rosin-esters,⁶² the advantages obtained compared to the use of ester-gum are not warranted on a cost basis.

While the earlier investigations described in the first and second periods were mainly concerned with 'straight' (unmodified) alkyd resins, and with attempts to improve these for use as coating media, bonding materials, and moulded products, no great commercial success was achieved, mainly on account of their slow rate of conversion to the insoluble and infusible state, i.e. the *C* form.

It would appear that this difficulty can now be overcome by the use of maleic anhydride instead of phthalic anhydride. S. L. M. Saunders⁶³ claims a process for the production of resins suitable for coating compositions which can be stoved at a temperature of about 130° by condensing a polyhydric alcohol with an unsaturated aliphatic polybasic acid and incorporating an oxygen-yielding polymerization catalyst such as benzoyl peroxide after the initial condensation has taken place. In contrast with succinic and phthalic acids which form long-chain non-convertible resins with a dihydric alcohol, and only yield a heat-convertible resin when combined with a polyhydric alcohol such as glycerol, maleic acid reacts with dihydric alcohols to form not only heat-convertible resins but also oxygen-convertible resins. Products varying from soft resins to balsams are obtained by condensing equimolecular proportions of maleic anhydride with different glycols, all of which readily gel on the application of heat in the absence of oxygen and, moreover, air-dry in the presence of a cobalt bimaleate catalyst. Gelation also occurs when films are exposed to ultra-violet light, giving rise to

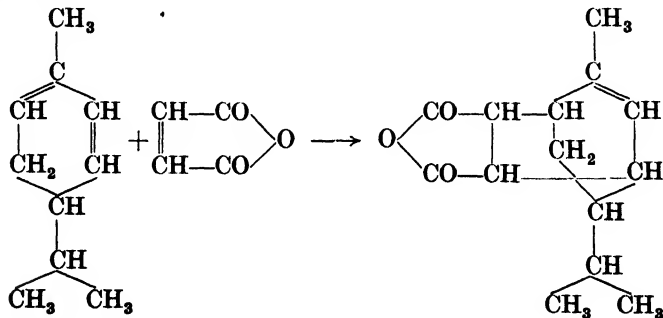
a typical gas-checked film familiar under similar circumstances with tung oil. It is considered that this conversion occurs through the double bonds of the maleic anhydride residue, by the union of a number of linear chains through the primary valence bonds arising from the double bonds, and not by secondary association forces. In support of this assumption it is shown that there is a loss of unsaturation according to bromine absorption measurements when polymerization takes place.⁶⁴

The polymerization of these resins is shown to involve two types of reactions⁶⁵—condensation and addition reactions, both of which occur simultaneously at elevated temperatures. Addition-polymerization, however, has been effected in the absence of further condensation polymerization, as indicated by little or no change in acid number, by exposure of the low condensed products to ultraviolet light and oxygen, when it has been found that addition-polymerization will not take place until condensation has progressed sufficiently far to provide a linear unit, which has at least two double bonds per molecule. The structure of triethylene maleate (prepared from equimolecular quantities of triethylene glycol and maleic anhydride) at the degree of condensation where addition-polymerization first takes place with conversion into a gelled product is represented by:



where R represents the grouping $-(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2-$.

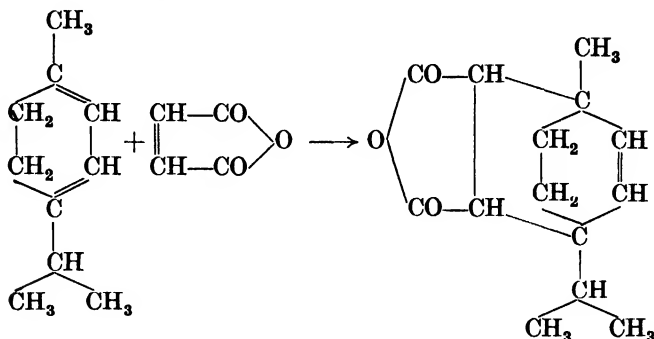
Another development during this fourth period again involves the use of maleic anhydride. O. Diels and K. Alder in pursuing their studies of the combination of maleic anhydride and similar compounds with conjugated double bonds investigated the use of certain terpenes and showed that α -phellandrene reacted with maleic anhydride to give high yields of a cyclic derivative of the following composition:⁶⁶



according to the normal Diene synthesis.

The reaction between α -terpinene and maleic anhydride was found

to yield resinous combination products,⁶⁷ and Diels, Alder, and Kech⁶⁸ showed that only about 50 per cent. yield of the cyclic derivative was obtained and recorded, in addition to the formation of a resinous non-volatile by-product.



(For an alternative formula cf. Chapter XIII (Miscellaneous Resins), p. 366.)

Further investigation⁶⁹ of these reactions showed that in both the case of α -phellandrene and α -terpinene, definite quantities of polymeric products were obtained in addition to the monomeric cyclic derivatives, which amounted to about 10 per cent. in the case of the α -phellandrene and about 50 per cent. in the case of the α -terpinene polymer. The respective molecular weights of the α -phellandrene and α -terpinene polymers were found to be 1,220 and 350 as compared to 234 for the monomer in each case. It was shown that the polymers as well as the monomer possessed an anhydride structure.⁷⁰

The Hercules Powder Co. have thus produced on a commercial scale a new polymeric polybasic acid termed 'Petrex' which can be employed instead of phthalic anhydride for the manufacture of alkyd resins, both of the modified and unmodified types.⁷¹ It has also been disclosed by the same company that certain terpene hydrocarbons not containing any conjugated double bonds will also combine with maleic anhydride such as dipentene⁷² and pinene⁷³ to yield resinous products which may be esterified and modified in much the same manner as those derived from α -pinene. Generally speaking, such esterified products are harder than the corresponding phthalic anhydride resins and possess a more complex structure, which may be accounted for by the fact that in the case of the terpinene-maleic anhydride base the alkyd molecule is a more branched chain polymer than that from phthalic anhydrides. Furthermore, such alkyd resins show a greater white spirit-compatibility and oil-solubility than the corresponding phthalic anhydride resins, apparently due to the terpene complex with which it is combined, and in this connexion it is interesting to compare the solubilizing action in oils of certain phenol-formaldehyde resins modified with terpenes.⁷⁴ Such resins

have found considerable application in the manufacture of roller-coating enamels and tin-printing finishes on account of their good adhesion and excellent flowing properties.

T. F. Bradley⁷⁵ in reacting equimolecular proportions of maleic anhydride and α -phellandrene, after separating the whole crystalline monomer, was able to obtain 16.5 per cent. yield of a non-volatile resinous substance, which was found to be mainly the anhydrides of tetra-carboxylic acids having an average molecular weight of 468 and a neutralization equivalent of 117. The resinous tri- or tetra-basic acid anhydrides obtained by Bradley after separating the dibasic anhydrides, however, were found to be capable of yielding heat-convertible resins with polyglycols, whereas non-convertible resins are obtained when such glycols are used to esterify the monomeric dibasic acids derived from terpenes and maleic anhydride. Furthermore, Bradley (*loc. cit.*) has been able to obtain tetra-basic acid anhydrides from dipentene and other non-conjugated terpenes in combination with maleic anhydride, and assumes that rearrangement first takes place with the formation of at least two dienes.

T. F. Bradley has also shown⁷⁶ that not only terpenes of the $C_{10}H_{16}$ series, but also polyterpenes corresponding to the formula $C_{20}H_{32}$ or higher polymers, will also react with maleic anhydride at temperatures of about 200° to yield acid resins which may be esterified and modified with rosin and fatty acids in a similar way. These polyterpene-maleic acid combination products, however, differ from those derived from the monoterpenes in that their glycol esters are heat-convertible and form infusible polymers on heating to 200 – 250° , whereas the monoterpene reaction products form non-heat-convertible glycol esters. If long-chain glycol polyesters are prepared they are found to be not only heat-convertible but also sufficiently flexible to be used as rubber substitutes in certain applications.

A still further development in the production of alkyd resins involving the use of maleic anhydride is due to its ability to combine with an unsaturated grouping in a drying oil and particularly with a conjugated grouping as in China wood-oil (*cf.* Chapter XIII (Miscellaneous Resins), p. 364). Carleton Ellis⁷⁷ showed that maleic acid would combine with China wood-oil, forming a viscous oil containing acidic groups, and it is assumed that the locus of coupling takes place through the conjugated double linkage which is opened up to form a 6-membered cyclic ring resulting in a derivative of phthalic acid. This 'maleinized' tung oil did not gel on heating to 282° after $1\frac{1}{2}$ hours, whereas tung oil itself will gel in 8 minutes at this temperature, and, moreover, it shows much less tendency to yield frosted films than that of the untreated oil. The slower drying of the 'maleinized' tung oil as compared to tung oil itself would indicate combination at the double bonds. Resinification of the 'maleinized' tung oil may be brought about by esterification with a polyhydric alcohol, in which case gelation occurs before esterification can be taken very far, resulting in products of high acid value. The

'maleinized' tung oil may also be used as an ingredient in the preparation of oil-modified alkyd resins in conjunction with phthalic anhydride and other dibasic acids or anhydrides. (Cf. Chapter XIII (Miscellaneous Resins), p. 364.)

Carleton Ellis claims⁷⁸ that cashew-nut shell oil will form an acidic resin with maleic acid which is capable of esterification with glycerol and other alcohols. E. A. Bevan and J. R. Tervet⁷⁹ have shown that it is not necessary for a conjugated linkage to be present in order to effect combination between maleic anhydride and an unsaturated oil, and that combination may be obtained with such widely differing degrees of unsaturation as olive, soya-bean, and linseed oils. Esterification, however, of such combination products with polyhydric alcohols, as in the case of wood-oil, cannot be taken very far before gelation occurs. It has been noted in this case, as with the straight alkyds and rosin-modified alkyds, that fumaric acid tends to yield products of higher viscosity or melting-point than its *cis*-isomer maleic acid.

The production of fumaric acid by a new fermentation process has so lowered its cost that comparison is now possible with maleic acid⁸⁰ as a raw material for synthetic resins. According to Doscher and co-workers, fumaric esters (diethyl, diallyl, and diethylene glycol) polymerize readily in the presence of suitable peroxide catalysts to form turbid or coloured thermo-plastic or thermo-setting resins, according to conditions, and these resins are improved by co-polymerization with vinyl derivatives. Condensation products of fumaric acid with glycols (diethylene glycol) can be polymerized in the presence of benzoyl peroxide at 100–200° to give hard and tough resins which can be machined and cast. Co-polymerization with vinyl benzene increased the hardness, and by varying the quantity and type of the co-polymer, e.g. diallyl fumarate, a wide range of resins can be obtained. Coating compounds, soluble in acetone, can be polymerized at 100° with an oxidizing catalyst, and addition of vinyl acetate increases the hardness. When incorporated with various fillers, e.g. gypsum or asbestos, linoleum-like or hard and tough plastics can be obtained from diethylene glycol fumarate, diallyl fumarate, and 0.1 per cent. benzoyl peroxide.⁸⁰

THE MANUFACTURE OF OIL-MODIFIED ALKYDS

The production of oil-modified alkyds, which up to the present time represents practically the entire manufacture of alkyd resins, is generally carried out either by the fatty acid or the alcoholysis process. The advantages of the latter process are obvious in that the fatty oil can be used directly as a basic ingredient without the preliminary process of splitting it into free fatty acids, and, further, the amount of glycerol required for the complete condensation is less by that amount already combined in the fatty glyceride. The alcoholysis processes as disclosed by the I.G.,⁸¹ by the British Thomson-Houston Company,⁸¹ Du Pont,⁸² and S. L. M. Saunders⁸³

suffer, however, from certain limitations as to the range of compositions which can be obtained from such processes; a monoglyceride containing two free hydroxyl groups if completely esterified with phthalic anhydride will yield a resin whose oil length is approximately 60 per cent. and short-oil resins in the region of 30 per cent. oil length could not be produced by the straightforward alcoholysis of a fatty oil. Longer oil lengths could be produced by the addition either during or after the reaction of further quantities of free fatty oils. The fatty acid process is not limited in this way and the whole scale of oil lengths can be produced by this method. S. L. M. Saunders,⁸⁴ however, overcame this difficulty by first preparing a partial ester containing at least two free hydroxyl groups of a polyhydric alcohol and an acid derived from a vegetable oil and adding thereto the incomplete condensation product of a polybasic organic acid and a polyhydric alcohol, and completing the condensation reaction. A vegetable oil may also be present as such if desired, and in this way the whole range of oil lengths could be produced by the alcoholysis process.

It is concluded that the general molecular structure of the condensation products obtained according to the fatty acid or fatty oil processes are similar, but the resins obtained by alcoholysis possess a slightly slower 'set time' with correspondingly better 'through' drying properties and slightly better durability than the fatty acid type.⁸⁵

The use of fatty acids either in the fatty acid process or as a starting-point in the manufacture of a partial ester possesses some advantages over the use of a fatty oil. I.C.I.⁸⁶ describe a process whereby fatty acids which have been fractionally distilled under reduced pressure are employed which give rise to very pale-coloured resins.

The production of oil-modified alkyds, although theoretically simple, involves a considerable number of simultaneous side reactions which affect the molecular structure and complexity of the final condensation product, which again materially affect their film-forming characteristics and behaviour. The control of these factors has necessitated considerable alteration and complication of plant design from the early manufacture in open varnish pots.

Reaction vessels are usually of the closed type constructed of aluminium or stainless steel, with mechanical agitation. Heating may be from direct gas- or oil-fired burners, by indirect heat-transfer systems using jacketed vessels, or by electricity using internal or external heating elements.

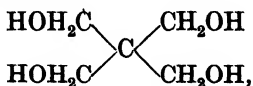
While the use of carbon dioxide for the provision of an inert atmosphere to obtain light-coloured products has been common practice,⁸⁷ the control of its rate of flow to assist the elimination of water and of waste products is an essential factor for uniform production. A process described by W. H. Peters⁸⁸ employs a degree of vacuum equivalent to not more than 2 in. of mercury during the latter stages of heating in order to remove surplus phthalic anhydride

and waste products without the necessity of raising the temperature to such a point as to cause decomposition of the resin. The water vapours removed under vacuum may be separately condensed and measured so as to give an indication of when the reaction is complete.

The possibility of employing electrical methods for controlling alkyd resin manufacture is suggested by R. H. Kienle and H. H. Race,⁸⁹ who have found that the direct-current resistance of 'glyptal melts' during preparation increased up to gelation point and was closely related to the degree of esterification. The use of copper in solution is said to produce products of low acid value,⁹⁰ and the addition of 0.00025–0.00035 per cent. of copper carbonate to the reacting ingredients is claimed to produce more light-stable resins.⁹¹

L. Blumer⁹² describes a process whereby uncombined initial materials and low molecular condensation products are removed at an intermediate stage of the condensation by dissolving in a hot alcoholic solvent. The solution separates into two layers and the upper layer containing the low molecular condensation products is removed, the acid value of the resin thereby being reduced. Progress in plant design and control has led to much greater degrees of esterification⁹³ with the result that products of lower acid value and better pigment compatibility have become available.

The formation of the partial esters by alcoholysis of the fatty oil may be promoted by catalysts such as soaps, alcoholates, and alkaline materials which are capable of reacting with fatty acids to form soaps.⁹⁴ C. W. A. Mundy⁹⁵ describes a process in which a pre-heated fatty oil is reacted with glycerol at a temperature slightly under the boiling-point of glycerol (290°), the process being self-catalysed. Any water formed in this process, which is conducted in an inert atmosphere, is removed by maintaining a slightly reduced pressure. By this means pale-coloured products containing a high proportion of monoglycerides (96–100 per cent.) are obtained. While glycerol is the polyhydric alcohol normally used, other polyhydric alcohols can be employed. I.C.I.⁹⁶ claim the use of a mixture of alcohols, one of which is a polyhydric alcohol, in order to produce resins of low acid value; examples quoted are mixtures of glycerol and ethylene glycol, glycerol and butyl alcohol, and glycerol and cyclohexanol. A similar process described by the British Thomson-Houston Company⁹⁷ claims the use of mixtures of glycerol with a dihydric alcohol for the production of more completely esterified resins which do not 'liver' with pigments. The use of polyhydric alcohols containing 4–6 hydroxy groups, for example, sorbitol and penta-erythritol, are claimed by the I.G.⁹⁸ Penta-erythritol is unique in containing four primary alcohol groups:

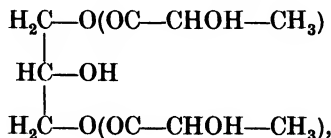


and is more reactive than glycerol, mannitol, or sorbitol on condensation with phthalic anhydride. The Atlas Powder Co.⁹⁹ claim

the use of an inner ether derived from a straight-chain hexahydric alcohol. The effect of the use of penta-erythritol and mixtures of penta-erythritol with glycerol in the condensation of a 50 per cent. linseed oil-modified alkyd is shown by L. K. Scott⁹³ in the following table:

Resin	Alcohol used	Viscosity at 50% solids on Gardner-Holdt standards	Solvent	Air-drying properties
1	Glycerol	U	Mineral spirits	Good
2	90% glycerol 10% penta-erythritol	W	„ „	Better than 1
3	80% glycerol 20% penta-erythritol	T	60% solvent naphtha 40% mineral spirits	Some better than 2
4	100% penta-erythritol	Product gelled		
5	24% glycerol 38% penta-erythritol 38% ethylene glycol	T	Mineral spirits	Equal to 1

Polyhydric alcohols having at least five carbon atoms and two or three $-\text{CH}_2\text{OH}$ groups attached to a single carbon atom such as dimethylol dimethyl methane, $\text{CMe}_2(\text{CH}_2\cdot\text{OH})_2$, are claimed by the Du Pont de Nemours Co.¹⁰⁰ Such polyhydric alcohols may in general be prepared by condensing formaldehyde with aldehydes and ketones having at least three carbon atoms and one or more hydrogen atoms in the α position to the carboxyl group. Glycerol can be esterified with lactic acid, yielding esters containing the same number of hydroxyl groups as were originally present in the polyhydric alcohol. J. J. Stearn, B. Makower, and P. H. Groggins¹⁰¹ have shown that glycerol di-lactate will form alkyd resins on condensation with polybasic acids. Glycerol di-lactate, the suggested formula for which is



possesses no primary alcohol groups and therefore it is expected that each alcoholic group would react with equal rapidity. Such condensation products are likely to possess more branched chains and gel at a lower average molecular weight than the corresponding glycerol condensation product.

Although phthalic anhydride on account of its commercial availability still remains the most widely used polybasic acid component, nevertheless the use of maleic acid or anhydride is reaching appreciable proportions, and reference has already been made to its use and that of 'Petrex' acid. Other acids, however, are employed to a minor degree. Adipic acid,¹⁰² succinic and diglycollic acids¹⁰³ are

claimed by the I.G. Kurt Albert¹⁰⁴ claims the production of plastic masses by the use of aliphatic polybasic acids containing more than six carbon atoms and particularly sebacic acid, while adipic, pimelic, suberic, azelaic, and sebacic acids are especially mentioned by H. A. Bruson.¹⁰⁵ Fatty oils may be oxidized to a mixture of monobasic and dibasic acids and condensed with polyhydric alcohols.¹⁰⁶ The condensation of aliphatic polybasic acids containing not more than three carbon atoms with polyhydric alcohols and non-drying alcohols are stated to be particularly suitable as plasticizers,¹⁰⁷ and the use of a substituted succinic acid in which at least one methylene group is connected by an aliphatic carbon atom which forms part of a residue containing at least five carbon atoms, for example nonenyl succinic acid, is stated to yield alkyd resins of improved solubility in volatile solvents.¹⁰⁸

The effect of altering the molecular ratio of phthalic anhydride to glycerol in a 50 per cent. soya-bean oil-modified alkyd is illustrated by L. K. Scott⁹³ in the following table:

<i>Mol. ratio phth./glyc.</i>	<i>Acid values of base resin</i>	<i>Viscosity of 50% solution</i>	<i>Drying time, titanium pigmented enamels</i>
1.2/1	7.42	13 poises	Best dry Sward-Rocker hardness = 22 in 24 hours
1.3/1	12.5	13 "	3rd slight tack in 24 hours
1.4/1	18.2	8.8 "	4th definite tack in 24 hours
1.5/1	23.5	8.0 "	Poorest. Very definite tack in 24 hours
(theoretical)			
1.6/1*	35	11.5 "	4th definite tack in 24 hours
1.7/1*	47.0	13 "	2nd dry Sward-Rocker hardness = 16 at 24 hours. Phthalic anhydride crystals on film

* Cooked for a shorter period to prevent gelation.

Of the fatty acids and fatty oils used to modify the alkyd condensation, oleic acid,²⁰ stearic acid,¹⁰⁹ and castor oil,¹¹⁰ were amongst the first to be mentioned. The latter, on account of its hydroxy group, can be incorporated directly into an alkyd resin condensation without first forming the free fatty acids or monoglyceride. W. Baird and E. E. Walker¹¹¹ have made use of this result as a means of subsequently incorporating a non-hydroxylated oil such as linseed oil. Amongst other non-drying oils and fatty acids are specifically mentioned cotton-seed oil,¹¹² coconut oil fatty acids, and mixtures of it with stearic or palmitic acid,¹¹³ and coconut oil itself.¹¹⁴ Generally, the flexibility of the condensation product increases with increase in molecular weight of the modifying fatty acid or oil, and for acids of the same carbon content the unsaturated acids yield more flexible resins than the saturated acids. Thus, whereas stearic acid yields a wax-like product, oleic acid yields a soft plastic resin.¹¹⁵ P. H. Fawcett¹¹⁶ suggests that the higher the degree of saturation of the fatty acid component the more soluble will the resin be in

the usual lacquer solvents. Of the drying oils, linseed, perilla, and China wood-oils are in common use. Blown oils and fish oils may be used,¹¹⁷ and the use of walnut oil¹¹⁸ and pure β -elaeostearic acid¹¹⁹ are specifically mentioned. It is, however, with the semi-drying oils that the alkyd resin condensation is shown to greatest advantage. Oils, such as soya-bean oil, which do not dry in the normal manner to a tough tack-free film and are relatively useless in oil-varnish manufacture, when used to modify an alkyd resin yield products which possess such a marked improvement in drying time that even tack-free films may be obtained on air-drying. This improvement in drying time is more marked the lower the degree of saturation of the oil. China wood-oil, which, however, shows less effect as regards improvement in drying time in alkyd resins than in orthodox varnish films, is nevertheless widely used for the water resistant properties which it conveys.¹¹⁵ The semi-drying oils possess other advantages in alkyd resin formulation due probably to the absence or low proportion of linolenic acid, namely that of resistance to after-yellowing either on exposure to high temperatures or on exposure to light or dark, and to the absence of wrinkle formation in stoved films. Sunflower-seed fatty acids¹²⁰ are particularly mentioned in these respects. Dehydrated castor oil is finding increasing use in the manufacture of alkyd resins owing to its resistance to discoloration, but nevertheless such products suffer from a tendency to 'gas check' under foul stoving conditions. Dehydration of the castor oil may be carried out at any rate partially, simultaneously with its condensation with glycerol and phthalic anhydride. H. Hönel¹²¹ describes such a process by reacting the three ingredients at a temperature of 260–70°, or by first reacting the castor oil with phthalic anhydride at above 200°, more than 1 molecule of anhydride to 2 molecules of oil being employed, and then esterifying with a polyhydric alcohol.¹²²

By heating together a glyceryl phthalate condensation product with colophony, copals, or ester gums solubility in fatty oils and petroleum distillates is obtained,¹²³ and products which can be combined with drying oils are obtained by condensing a polyhydric alcohol with a mixture of a polybasic acid and one or more natural resins or gums.¹²⁴ The further modification of a fatty acid modified alkyd condensation with an acid resin such as colophony is described by R. L. Yeates,¹²⁵ and in a similar manner the incorporation of a masticated copal such as that from Congo, Benguela, Pontianak, Manila, and Kauri is claimed by Beck, Koller.¹²⁶ The combination of a non-drying oil-modified alkyd with rosin is described by Du Pont¹²⁷ and a drying oil-modified alkyd in which the amount of colophony exceeds the amount of the oil by 15 per cent. by weight is claimed by I.C.I., Ltd.¹²⁸ A natural resin may also be incorporated directly by heat with a drying oil-modified alkyd of 50 per cent. oil length in the absence of solvent.¹²⁹ Shellac also may be used as a modifying agent.¹³⁰ While the introduction of abietic acid has a profound effect in detracting from the characteristic durability

of a 'straight' drying oil-alkyd,¹¹⁵ nevertheless the resins possess improved oil- and varnish-solubility and hardness, and, further, their alkali-resistance is improved, since such esters are less readily saponified.⁸⁶

The further modification of oil-modified alkyd resins with a phenol formaldehyde resin produces certain very desirable features, and the products combine to some extent the through-drying properties and water resistance of the phenol-formaldehyde type with the quick-drying and durable characteristics of the alkyd type of resin. I.C.I.¹³¹ employs purified resoles, whereas Hönel¹³² uses the low molecular condensation products comprising mainly phenol alcohols obtained by the alkaline condensation with formaldehyde of phenols in which not more than two of the three reactive positions *ortho*-, *ortho*-, and *para*- to the phenolic group are unsubstituted, for example, *p*-tertiary butyl phenol. Such resoles are capable of reacting with any ester without the necessity of a solvent or dispersing agent. S. L. M. Saunders¹³³ dissolves a fusible phenol aldehyde resin in a partial ester of a fatty acid and glycerol which contains at least two free hydroxyl groups and then continues the esterification with a polybasic acid. Du Pont¹³⁴ react a drying-oil solution of a phenol-formaldehyde resin with glycerol and subsequently esterify with a polybasic acid. Rosenblum¹³⁵ reacts a fusible phenol, aldehyde, or ketone resin with a polyhydric alcohol, which has already been partially neutralized with phthalic anhydride. Combination may also be effected by heating together in a closed vessel a phenol, formaldehyde, polyhydric alcohol and a polybasic acid,¹³⁶ or by heating together a phenol, drying oil, polyhydric alcohol and a polybasic acid, and the resulting product being heated with an aldehyde in the presence of a catalyst such as ammonia.¹³⁷

The modification of an alkyd resin with a urea-formaldehyde resin was described by S. Goldschmidt and R. Mayrhofer¹³⁸ and later developed by A. G. Hovey and T. S. Hodgins¹³⁹ and extended to oil-modified alkyds by I.C.I., Ltd.¹⁴⁰ Such products possess superior light-fastness to those of the phenol-modified type.

THE APPLICATION OF ALKYD RESINS

The use of alkyd resins has been almost entirely confined to coating compositions, for which their film-forming properties make them particularly adaptable. While certain properties of the simple or 'straight' alkyd at first directed attention to the possibility of their application in the plastics and moulding industries, the long time required for conversion to the *C* form hindered any appreciable development in that direction; nevertheless, owing possibly to the fact that these resins owed their initial development to the electrical industry, some successful development has taken place in that field (cf. Chapter XIV).

The rapid development of alkyd resins during the last ten years is entirely due to their use in large and ever-increasing quantities

by the paint, varnish, and lacquer industries. For the purpose of these applications it is convenient to divide the alkyd resins into two types, namely, convertible and non-convertible types, according to whether their films are capable of being changed to an insoluble state either by heat or oxidation, and thus are of value as the sole film-forming medium, or whether they remain unchanged by such processes and are employed as adjuncts with other film-forming materials. In the latter class are included the non-drying oil-modified alkyds, rosin-modified glycerol phthalate, and glycerol maleate condensation products, and those alkyds employing a proportion of mono- or dihydric alcohols. The non-drying oil-modified alkyds are employed in nitrocellulose lacquers on films of which they confer great durability. One advantage of this type of resin lies in its opacity to actinic light, to the action of which clear cellulose lacquers are particularly vulnerable. In pigmented lacquers this property is also beneficial, as it protects the pigment from those rays which are mainly responsible for the fading of colours.¹⁴¹ The resins are generally compatible with nitro-cotton in all proportions, and the resin content of the lacquer may exceed that of the nitrocellulose, as these resins do not render the film brittle,¹⁴² thus permitting the formulation of lacquers of high solid content even when employing a high viscosity nitro-cotton.

A typical formula for the non-volatile portion of a clear finishing lacquer is alkyd resin 250 parts, dry nitro-cotton 100 parts, and dibutyl-phthalate 60 parts. Such lacquers possess exceptional toughness, adhesion, and resistance to oil and alcohol in addition to durability on exposure to weather, and, moreover, will not lift under ordinary conditions when successive coats are applied. H. Brendel¹⁴³ considers that nitrocellulose lacquers containing alkyd artificial resins remain almost intact after an outside exposure of seven months; the durability of films containing this type of resin is not a function of the viscosity of the nitrocellulose, a comparatively low proportion of which should be used. The introduction and development of the etherified urea-formaldehyde resin for baking finishes has also extended the field of application of the non-drying oil-modified alkyd which are employed to plasticize finishes of this type.

The rosin-modified, glycerol phthalate and glycerol maleate condensation products, although originally developed for use in cellulose ester lacquers, are now finding application in the manufacture of oil varnishes, particularly in the case of the rosin maleic esters. W. E. Wornum¹⁴⁴ discusses the behaviour of such a typical resin-oil system at different temperature levels and time periods. In nitrocellulose lacquers these resins impart a high gloss, hardness, excellent sanding properties, and resistance to oils and alcohol. They do not impart durability to a lacquer film, and are thus employed for indoor finishes and particularly for sanding sealers and wood lacquers.

Compatibility of resins with cellulose acetate is much more difficult to effect than with nitrocellulose, but certain alkyds in which di-

hydric alcohols are employed in the condensation can be incorporated successfully in cellulose acetate lacquers.¹⁴⁵

While early efforts were directed towards employing a straight glyceryl-phthalate resin as the basis for stoving finishes, these met with little success on account of the high temperatures required for conversion to the *C* stage to take place. As already described,⁶³⁻⁵ this difficulty can be overcome by the replacement of phthalic anhydride by maleic anhydride in the production of the condensation product.

It is, however, the drying oil-modified type of resin which has almost revolutionized the paint, varnish, and lacquer industry, not only by the production of new finishes hitherto thought to be impossible, but by the setting up of an entirely new standard of durability. H. H. Morgan in 1932¹⁴⁶ in reviewing the position finds that, as a result of exposure tests extending over eighteen months, synthetic finishes of this type are superior in durability and retention of gloss to natural resin varnishes of corresponding quality. He points out that the rapid surface-hardening of these finishes is of great importance as regards the reduction of the period during which dirt may become permanently adherent to the surface, and also because it is during the early portion of its life-history, before it attains final stability, that the film is particularly susceptible to destructive agents, especially moisture.¹⁴⁷ R. H. Kienle and C. S. Ferguson¹⁴⁸ arrive at similar conclusions as a result of their experiments. The drying oil-modified alkyd was found to give films of higher durability and shorter drying time than the older type of lacquer and varnish. The resistance of the film to oils and solvents generally was also higher than in the case of oil varnishes. These workers also discuss the properties of stoving finishes based on this type of resin. Since those early investigations, many workers have substantiated those claims upon the basis of longer and more extended trials, and it is probably true to say that at the present time there is no other organic finish which provides the same degree of durability on exposure to weather as a correctly formulated drying oil-modified alkyd resin. F. J. Siddle points out¹¹⁵ that, whereas in an orthodox varnish its properties are essentially a mean of the characteristics of its components, the durability increasing with increasing oil length, within comparatively wide limits—30 to 65 per cent. drying oil—there is no marked difference in durability, as the oil content of a drying oil-alkyd varies. As a rough comparison he states that linseed oil-modified alkyds containing 60, 50, and 40 per cent. of oil respectively, approximate in flexibility to an orthodox varnish containing 85, 80, and 75 per cent. of oil respectively. The retention of that flexibility on ageing, however, is much better in the case of the alkyd than in the case of the oil varnish. A linseed oil-alkyd containing 35 per cent. of linseed oil approximates in drying time to an orthodox varnish containing only 15 per cent. of oil, and yet in durability is superior to 75 per cent. oil-length orthodox varnish. It must, of course, be stressed that the characteristics

of a paint or enamel film do not depend entirely upon those of the vehicle alone, and the correct pigmentation is necessary to obtain the maximum results from any given vehicle.

Depending upon the oil-length, type of oil, and degree of condensation, some alkyds are soluble in raw or bodied oils as well as compatible with orthodox-type varnishes, and are thus employed for reinforcing the durability characteristics, speed of drying, and hardness of such varnishes.

Nevertheless it must be admitted that in general films of pure drying oil-modified alkyds possess inferior resistance to water and alkalis than do high-grade oleo-resinous varnishes.⁹³ The following table compares the water permeabilities of some drying oil-modified alkyd films with those of two orthodox varnishes. Measurements were made in a Payne Cup at 38° of the number of mg. of water per sq. cm. per 24-hour period for 0.01 mm. thickness.

No.	Material	Oil	Dry	Permeability
1	Alkyd	40% linseed	Air-dry	49.4
2	"	55% "	"	57.9
3	"	70% "	"	74.1
4	"	40% "	Stove 1 hr. 250° F.	39.6
5	"	55% "	" "	44.4
6	Oleo-resinous phenolic	33 gal. tung oil	Air-dry	39.8
7	Oleo-resinous ester gum	33 " "	"	39.8

It is claimed that by reaction of the free hydroxyl groups with a keten ($R_2C:CO$) improvement in water-resistance is obtained.¹⁴⁹ Improvement can also be effected by the use of a proportion of China wood-oil in the condensation and modification with a phenol-formaldehyde resin.

C. S. Farmer¹⁵⁰ in discussing the problems associated with the use of alkyd resins considers their main advantages to be high order of durability, excellent pigment dispersion, yielding good gloss and flowing properties, accompanied by exceptional toughness and adhesion and relative uniformity, together with the removal of the need for prolonged tankage of the media before use. As a result alkyd resins are used almost exclusively or in increasing quantities in commercial vehicle,⁹⁹ cycle, toy, instrument, and tin-printing finishes for metal-priming coats, both air-dried and stoved, and in this connexion may be used by the 'wet-on-wet' application, and in conjunction with urea-formaldehyde resins for low-temperature stoving finishes.

On the other hand, such alkyd resins have not made the same headway in the field of decorative paints as in the industrial field. Gloss finishes formulated on the basis of a drying oil-modified alkyd for decorative purposes tend to be rather thin in consistency and to 'sag' on vertical surfaces unless applied with care, and the higher proportion of volatile thinners is liable to cause undesirably rapid setting under summer conditions. Moreover, the excellent pigment

dispersion obtained with alkyd resins may be accompanied by hard settling due to close packing of the settled pigment. By employing a long-oil alkyd as a grinding medium for the preparation of heavy pigment pastes, which are thinned with oleo-resinous varnishes, a compromise can be effected which makes some use of the excellent durability and dispersive power of the alkyd, and at the same time modifies their defective brushing properties and excessive flow.

Alkyd resins may be employed in the form of an aqueous emulsion as the basis for water paints.¹⁵¹ Such paints are of particular value for imparting great durability upon the surfaces of porous materials which tend to absorb water, and, moreover, dry quickly, their resistance against abrasion, weathering, and other corroding influences being excellent. Alkyd resins may also be converted into water-soluble products by treatment with ammonia or aliphatic amines, or with an aqueous solution of an alkali metal hydroxide.¹⁵² Films of such solutions may be rendered insoluble by treatment with acids and their use has been described for stiffening and proofing felt hats.¹⁵³

REFERENCES

1. R. H. Klenle and A. G. Hovey, *J. Amer. Chem. Soc.*, 1929, **51**, 509.
2. Drummond and Morrell, *Natural and Synthetic Resins*, p. 164.
3. R. H. Klenle and A. G. Hovey, *J. Amer. Chem. Soc.*, 1930, **52**, 3636.
4. R. H. Klenle and C. S. Ferguson, *Ind. Eng. Chem.*, 1929, **21**, 349.
5. H. Honel, *Kunst*, 1931, **21**, 105, 132; *Paint Oil and Chem. Rev.*, 1931, **91**, 19.
6. G. Bozza, *Giorn. Chim. Ind. Appl.*, 1932, **14**, 294, 400; *B.*, 1932, 1040.
7. W. E. Wornum, *J. Oil and Col. Chem. Assoc.*, 1933, **16**, 231.
8. Cf. p. 480 in chapter on the Problems of Resinification.
9. R. H. Klenle, P. A. van der Meulen, and F. E. Petke, *J. Amer. Chem. Soc.*, 1939, **61**, 2258.
10. *J.S.C.I.*, 1926, **45**, 190 T.
11. *J. Ind. Eng. Chem.*, 1919, **11**, 1031; 1922, **14**, 120.
12. Report No. 131, 1938, on Synthetic Resins and their Raw Materials, by the United States Tariff Commission.
13. *J. prakt. Chem.*, 1856, **69**, 85.
14. *Ann. chim. phys.*, 1863 (III), **67**, 313.
15. *J.S.C.I.*, 1901, **20**, 1075.
16. B.P. 3,271 (7 Feb. 1913).
17. U.S.P. 1,108,329 (25 Aug. 1914).
18. British Thomson-Houston Co., B.P. 22,544 (6 Oct. 1914).
19. U.S.P. 1,098,777 (2 June 1914).
20. B.P. 22,544 (26 Oct. 1914).
21. B.P. 24,254 (24 Nov. 1913).
22. U.S.P. 1,091,627 and 1,091,628 (31 March 1914).
23. U.S.P. 1,119,592 (1 Dec. 1914).
24. B.P. 9,985 (25 Sept. 1913) and U.S.P. 1,082,106 (23 Dec. 1913).
25. U.S.P. 1,085,112 (27 Jan. 1914).
26. U.S.P. 1,108,331 and 1,108,332 (25 Aug. 1914).
27. U.S.P. 1,413,144 (18 April 1922).
28. C. B. Downs and Louis Welsburg of the Barrett Company, U.S.P. 1,489,744 (8 April 1924).
29. U.S.P. 1,424,137 (25 July 1922).
30. B.P. 326,591 (11 Feb. 1926).
31. B.P. 250,949; *B.*, 1926, 988.
32. B.P. 235,589; *B.*, 1926, 414.
33. H. H. Morgan, *J. Oil Col. Chem. Assoc.*, 1932, **15**, 106.
34. U.S.P. 1,893,872; B.P. 284,349; *B.*, 1934, 78.
35. B.P. 318,003 (1930).
36. U.S.P. 1,888,849; B.P. 285,459; *B.*, 1933, 721.
37. U.S.P. 1,898,790; B.P. 370,440; *B.*, 1932, 614.
38. B.P. 360,173; *B.*, 1932, 235.
39. B.P. 318,014; *B.*, 1929, 827.
40. B.P. 364,737; *B.*, 1932, 315.
41. B.P. 235,595 (22 April 1926).
42. B.P. 327,946; *B.*, 1930, 677.
43. B.P. 352,981; *B.*, 1931, 1147.

44. B.P. 498,818; B., 1939, 634.
45. B.P. 492,934; B., 1939, 295.
46. I. Rosenblum, B.P. 453,228; B., 1936, 1167.
47. *Ibid.*, B.P. 461,742; B., 1937, 470.
48. *Ibid.*, B.P. 444,021; B., 1936, 511.
49. *Ibid.*, B.P. 457,494; B., 1937, 158.
50. S. L. M. Saunders, B.P. 498,818; B., 1939, 634.
51. *Ann.*, 1928, 460, 98; B.P. 300,130; B., 1930, 549; Carleton Ellis, *The Chemistry of Synthetic Resins*, 1935, vol. II, chap. 40.
52. U.S.P. 1,722,566; B., 1929, 826.
53. B.P. 303,388.
54. B.P. 327,095; B., 1930, 570.
55. U.S.P. 1,757,104; B., 1930, 1121.
56. Carleton Ellis, U.S.P. 1,722,566; B., 1929, 826.
57. L. F. Fieser, *Chemistry of Natural Products related to Phenanthrene* (Reinhold Publishing Co., 1937), 49-50.
58. L. Ruzicka and J. Meyer, *Helv. Chim. Acta*, 1922, 5, 315.
59. Oil and Colour Chem. Assoc. (Varnish Symposium), Harrogate, 1939).
60. I G Farbenind., A.-G., B.P. 355,281.
61. Carleton Ellis, U.S.P. 2,063,540, 2,063,541, 2,063,542; B., 1938, 1076.
62. B.P. 303,387.
63. B.P. 500,547; B., 1930, 405.
64. H. T. Vincent, *Ind. Eng. Chem.*, 1937, 29, 1267.
65. T. F. Bradley, E. L. Kropa, and H. S. Johnston, 1937, 29, 1270.
66. Diels and Alder, *Ann.*, 1927, 460, 98.
67. Hercules Co., U.S.P. 1,993,025; B., 1936, 287.
68. Diels, Alder, and Kech (Dissertation, Christian Albrecht University, Kiel, 1932).
69. E. R. Littmann, *J. Amer. Chem. Soc.*, 1935, 57, 586.
70. E. R. Littmann, *Ind. Eng. Chem.*, 1936, 28, 1150.
71. U.S.P. 1,993,026, 1,993,027, 1,993,028, 1,993,029, 1,993,030; B., 1936, 287.
72. U.S.P. 1,993,031, 2,047,004; B., 1936, 287; B., 1937, 1374.
73. U.S.P. 1,993,034; B., 1936, 287.
74. Rosenblum, B.P. 416,476; B., 1934, 1022.
75. T. F. Bradley, B.P. 484,697.
76. B.P. 483,908; B., 1938, 888.
77. U.S.P. 2,033,131 and 2,033,132; B., 1937, 471.
78. U.S.P. 2,033,133; B., 1937, 472.
79. B.P. 500,348; B., 1939, 405.
80. C. K. Doecher, J. H. Kane, G. O. Cragwall, and W. H. Staebner, *Ind. Eng. Chem.*, 1941, 33, 315.
81. B.P. 356,340; B., 1931, 1019.
82. B.P. 359,365; B., 1932, 119.
83. B.P. 432,103; B., 1935, 861.
84. B.P. 432,158; B., 1935, 861.
85. T. Fitzpatrick, *Paint, Oil, & Chem. Rev.*, Nos. 12 and 14, 1940.
86. B.P. 408,667; B., 1934, 547.
87. B.P. 320,041; B., 1929, 989.
88. B.P. 444,889; B., 1936, 704.
89. *Trans. Electrochem. Soc.*, 1934, 63, 231; B., 1934, 511.
90. B.P. 463,709.
91. B.P. 410,837; B., 1934, 686.
92. B.P. 406,444; B., 1934, 371.
93. L. K. Scott, *Official Digest*, 1940, 105.
94. B.P. 421,284; B., 1935, 194.
95. *J. Oil Col. Chem. Assoc.*, 1938, 21, 96.
96. B.P. 305,965; B., 1929, 333.
97. B.P. 317,797.
98. B.P. 330,910; B., 1930, 828.
99. B.P. 505,016.
100. B.P. 419,604; B., 1935, 112.
101. *Ind. Eng. Chem.*, 1940, 32, 1335; U.S.P. 2,181,321.
102. B.P. 328,728; B., 1930, 676.
103. B.P. 330,909; B., 1930, 828.
104. B.P. 341,447.
105. B.P. 363,859; 360,363; B., 1932, 438.
106. B.P. 377,265; B., 1932, 948.
107. B.P. 441,912; B., 1936, 337.
108. B.P. 464,276; B., 1937, 1312.
109. U.S.P. 1,098,766.
110. U.S.P. 1,098,728.
111. B.P. 335,292; B., 1930, 292.
112. B.P. 327,096; B., 1930, 570.
113. B.P. 356,141; B., 1931, 1019.
114. B.P. 397,554.
115. F. J. Siddle, Oil and Col. Chem. Assoc. (Varnish Symposium), Harrogate, 1939, p. 91.
116. *Off. Dig.*, 1932, No. 120, 1035.
117. B.P. 352,981; B., 1931, 1147.
118. B.P. 395,899; B., 1933, 837.
119. B.P. 341,012; B., 1931, 405.
120. B.P. 422,131; B., 1935, 240.
121. B.P. 431,495; B., 1935, 816.

122. B.P. 487,681.
123. B.P. 308,671; B., 1929, 484.
124. B.P. 308,387.
125. Grindley & Co. and R. L. Yeates, B.P. 306,924; B., 1929, 404.
126. B.P. 467,945; B., 1937, 940.
127. B.P. 377,724.
128. B.P. 391,508; B., 1933, 557.
129. B.P. 406,991; B., 1934, 413.
130. B.P. 468,542; B., 1938, 1070.
131. B.P. 308,048; B., 1929, 444.
132. B.P. 334,570.
133. B.P. 431,951; B., 1935, 861.
134. B.P. 437,894; B., 1936, 110.
135. B.P. 370,946; B., 1932, 808.
136. B.P. 308,966; B., 1932, 475.
137. B.P. 451,591; B., 1936, 1007.
138. B.P. 316,144.
139. B.P. 502,308.
140. B.P. 344,401; B., 1931, 597.
141. T. F. Bradley, *Off. Dig.*, 1931, p. 555, and *Oil and Col. Trades J.*, 1931, 750.
142. *Paint and Varnish Production Manager*, Nov. 1932, p. 32.
143. *Farben.-Chem.*, 1932, 3, 136; B., 1932, 613.
144. 'Varnish Making', *Oil and Col. Chem. Assoc.*, Harrogate Conference, 1939, p. 64.
145. B.P. 322,541, 322,542; B., 1930, 157.
146. *J. Oil Col. Chem. Assoc.*, 1932, 15, 206.
147. See also L. K. Scott, *Paint, Oil, & Chem. Rev.*, 1930, 90, 84; E. J. Probert, *Off. Digest*, 1930, No. 96, p. 128.
148. *Ind. Eng. Chem.*, 1929, 21, 349.
149. B.P. 419,373; B., 1935, 12.
150. *J. Oil Col. Chem. Assoc.*, 1940, 23, 364.
151. B.P. 344,458; B., 1931, 597.
152. B.P. 356,738, 358,095; B., 1931, 1062; B., 1931, 1147.
153. B.P. 358,104; B., 1931, 1135.

APPENDIX
SOME COMMERCIAL ALKYD RESINS

<i>Supplier</i>	<i>Base resin</i>	<i>Type of product</i>	<i>General uses</i>	<i>Solutions available</i>
Albert Pro-ducts Ltd.	Alprokyd 525 V	Non-drying oil-modified alkyd.	Cellulose lacquers.	70% solution in xylol.
	Alprokyd 607 P	Drying oil-modified alkyd. Long oil type.	Brushing decorative finishes.	..
Beck, Koller & Co. (England) Ltd.	Alprokyd 615 Z	Drying oil-modified alkyd. Medium oil length.	Quick-drying brushing types for decorative industrial finishes.	..
	Alprokyd 624 J	Drying oil-modified alkyd. Short oil type.	Stoving or air-drying spraying or dipping finishes.	60% solution in xylol.
	Alprokyd 626 L	Drying oil-modified alkyd. Medium oil length.	For high-speed decorative and industrial work, spraying or baking.	70% solution in xylol.
	High viscosity	"	For cooking with oils or varnish.	..
Beck, Koller & Co. (England) Ltd.	Alprokyd 626 L	"	Manufacture of oil varnishes and nitrocellulose lacquers.	..
	Low viscosity	Modified maleic type.	"	..
	Alresate 201 C	"	"	..
	Alresate 313 C	"	"	..
	Alresate 177 C	"	"	..
	Beckosol 1	Phenol-modified oil-extended alkyd.	Undercoats. Quick-drying and water-resistant air-drying and stoving finishes.	Beckosol 1; 50% in mineral spirits.
	Solid	"	"	Beckosol 1316X; 50% in xylol.
	Beckosol 3	Phenol-modified alkyd.	Quick air-drying and baking finishes. Spraying.	Beckosol 1303; 50% in xylol.
	Solid	Non-phenolic modified alkyd.	Air-drying interior finishes of good colour. Roller-coating enamels.	Beckosol 1320; 50% in xylol.
	Solid	Long oil type.	Stoving, spraying finishes.	Beckosol 1319; 80% in mineral spirits.
Beckosol 7	Drying oil-modified alkyd.	Stoving, spraying finishes.	Beckosol 1307; 50% in xylol.	
Solid	"	Quick air-drying and stoving finishes for spraying.	Beckosol 1313; 46% in H.F. naphtha.	
Solid	"	"	"	

<i>Supplier</i>	<i>Base resin</i>	<i>Type of product</i>	<i>General uses</i>	<i>Solutions available</i>
Beck, Koller & Co. (England) Ltd. (cont.)	Beckosol 14; Solid.	Drying oil-modified alkyd.	Air-drying and stoving brushing or spraying finishes.	Beckosol 1331; 80% in mineral spirits.
	Beckosol 15; Solid.	" "	For cooking with oils and varnishes.	..
	Beckosol 18; Solid.	" "	Brushing or spraying finishes, cooking into varnishes.	Beckosol 1318; 80% in mineral spirits.
	Beckosol 23; Solid.	Non-drying oil-modified alkyd.	Nitrocellulose lacquers. Urea-formaldehyde finishes.	Beckosol 1323 X; 50% in xylol.
	Beckosol 24; Solid.	" "	Nitrocellulose lacquers.	Beckosol 1324; 80% in toluol.
	Beckosol 27; Solid.	Drying oil-modified alkyd.	Brushing air-drying finishes.	Beckosol 1427; 80% in mineral spirits.
	Beckosol 30; Solid.	Pure phenol-modified alkyd.	Air-drying brushing enamels.	Beckosol 1430; 50% in mineral spirits.
	Beckosol 31; Solid.	Non-drying oil-modified alkyd.	Nitrocellulose lacquers.	Beckosol 1308 X; 50% in xylol.
	Beckosol 33; Solid.	Drying oil-modified alkyd.	Air-drying brushing stoving and spraying finishes.	Beckosol 1333; 45% in xylol.
	Beckosol 34; Solid.	" "	Air-drying stoving brushing or spraying finishes.	Beckosol 1334; 50% in mineral spirits.
Beckolin.	" "	Grinding medium. Can be cooked into oils and varnishes.	..	
Beckacite K 100 E.P.	Modified maleic type.	} Oil varnishes and nitrocellulose lacquers.	..	
Beckacite K 100 P.	" "		..	
Beckacite K 125.	" "		..	
Beckacite 1111.	" "		..	
Erinite, 1000.	Drying oil-modified alkyds.	
Erinite, 1000 PA.	Medium oil length.	
Erinite, 1001.	Drying oil-modified alkyds.	
Erinite, 1001 PA.	Long oil length.	
R. H. Cole & Co. Ltd.	Erinite, 1000.	Drying oil-modified alkyds.
	Erinite, 1000 PA.	Medium oil length.
	Erinite, 1001.	Drying oil-modified alkyds.
	Erinite, 1001 PA.	Long oil length.

<i>Supplier</i>	<i>Base resin</i>	<i>Type of product</i>	<i>General uses</i>	<i>Solutions available</i>
R. H. Cole & Co., Ltd. (<i>cont.</i>)	Erinte alkyd, 1002.	Non-drying oil-modified alkyd.	..	70% solution in xylol.
	Erinte alkyd, 1003.	" "	..	70% solution in xylol.
	Erinte, 200.	} Modified maleic types.
	" , 201.	
	" , 202.	
F. A. Hughes & Co., Ltd.	Celestol, A.	Pure drying oil-modified alkyd.	Fast air-drying and low-temperature stoving enamels.	..
	Celestol, B.	" "	Air-drying enamels of great flexibility. Blending vehicle.	..
	Celestol, D.	" "	Clear protective finishes resistant to water spotting. Air-drying enamels of great durability.	..
	Celestol, H-1.	" "	High-temperature white stoving enamels.	..
	Celestol, 575.	" "	Fast white air-drying and stoving enamels.	..
	Celestol, 830.	" "	Fast air-drying and low bake enamels. N.C. lacquers.	..
	Celestol, 2195.	Pure non-drying oil-modified alkyd.	N.C. lacquers.	..
	Celestol, 562.	Phenol oil-modified alkyd.	Hard water-resistant air-drying and low-temperature stoving enamels.	..
	Celestol, 747.	Phenol-modified alkyd.	White-spirit soluble type of Celestol 562.	..
	Paranol, L.B. 1.	Modified maleic type.	Nitrocellulose lacquers, stoving oleo-resinous varnishes.	..
	Paranol, L.B. 89.	" "	" "	..
	Paranol, 1639.	" "	Sanding sealers. " Printing inks. White stoving enamels.	..

<i>Supplier</i>	<i>Base resin</i>	<i>Type of product</i>	<i>General uses</i>	<i>Solutions available</i>
Imperial Chemical Industries, Ltd.	Paralac, 15.	Drying oil-modified alkyd.	Brushing decorative finishes. Printing inks.	80% solution in turpentine.
	Paralac, 17.	" "	Air-drying brushing finishes, re-inforcing resin, gloss paints.	" "
	Paralac, 18.	" "	Air-drying or stoving, spraying finishes.	60% solution in xylol. 53% solution in turpentine. 70% solution in butylalcohol. 60% solution in xylol.
	Paralac, 19.	" "	General industrial stoving finishes.	" "
	Paralac, 20.	" "	Low bake spray or dipping finishes.	" "
	Paralac, 285.	Non-drying oil-modified alkyd.	Plasticizer for nitrocellulose lacquers and urea-formaldehyde resins.	50% solution in xylol.
	Paralac, 585.	" "	Nitrocellulose lacquers.	" "
	Paralac, 685.	" "	" "	" "
	Paralac, 385.	" "	" "	" "
	Bedesol, 52.	Rosin-modified alkyd.	" "	" "
Scott Bader & Co., Ltd.	Paralacs, 1001, 1101, 1201.	Thermo-hardening free from drying oils, rosins, or phenolic resins.	Bonding for asbestos, mica.	" "
	Synolac, SB. 144.	Drying oil-modified alkyd.	Non-yellowing varnishes and white enamels for air or stove-drying; cellulose lacquers.	In xylol or mineral spirits.
	Synolac, SB. 145.	" "	Stoving finishes where extreme resistance to yellowing required.	" "
	Synolac, SB. 148.	Linseed-oil-modified alkyd.	Outdoor enamels, spray finishes, stoving finishes, and primers.	In xylol or mineral spirits.
	Synolac, SB. 546.	Drying oil-modified maleic type.	Paints and varnishes of exceptional hardness, water resistance, and colour retention.	" "

Supplier	Base resin	Type of product	General uses	Solutions available
Scott Bader & Co., Ltd. (cont.)	Synolac, SB. 147.	Linseed oil-modified alkyd.	General paints and varnishes, printing inks. Primer for anti-corrosive paints. (Use with SB. 148 to get faster drying primers.)	..
	Synolac, SB. 150.	" " "	General paints and varnishes, printing inks.	..
	Synolac, SB. 542.	Drying oil-modified maleic type.	General paints and enamels of excellent colour retention.	..
	Synolac, SB. 1442.	Phenol-modified alkyd.	General paints and enamels of the rapid-hardening and water-resistant type.	In xytol or mineral spirits.
	Synolac, SB. 102.	Modified alkyd.	Bonding agent for mica, lacquers, rubber-stereo printing inks, spirit varnishes.	..
	Synolac, SB. 121.	Natural resin-modified alkyd.	Cellulose lacquers, wood lacquers, sanding sealers.	..
	Synolac, SB. 164.	Non-drying oil-modified alkyd.	General purpose cellulose lacquer resin, car finishes, wood lacquers.	In xytol or mineral spirits.
	Synolac, SB. 166.	" " "	Nitrocellulose lacquers.	" " "
	Synolac, SB. 565.	Non-drying oil-modified maleic type.	Non-yellowing resin plasticizer for cellulose lacquers and urea resins.	" " "
	Synolac, SB. 149.	Drying oil-modified alkyd.	Hard enamels, industrial finishes, stoving primers. N.C. finishes.	" " "
	Crestanol, SB. 526.	Modified maleic type..	Oil varnishes and nitrocellulose lacquers.	..
	Crestanol, SB. 524.	" " "	" " "	" " "
	Crestanol, SB. 523.	" " "	" " "	" " "
	Crestanol, SB. 522.	" " "	" " "	" " "

<i>Supplier</i>	<i>Base resin</i>	<i>Type of product</i>	<i>General uses</i>	<i>Solutions available</i>
Bakelite, Ltd.	Rezyl, 14, 99.	Non-drying oil-modified alkyds.	Cellulose lacquers.	..
	Rezyl, 420.	Drying oil-modified alkyd.	High-temperature stoving finishes, resistant to discoloration.	..
	Rezyl 412.	" "	Low-temperature stoving finishes, resistant to discoloration.	..
	Rezyl, 880.	" "	Architectural white finishes.	..
	Rezyl, 869.	" "	Brushing enamels of good colour retention.	..
	Rezyl, 114.	" "	Quick-drying finishes.	..
	Rezyl, 775.	Phenol-modified alkyd.	Primers.	..
	Teglac, 15.	Rosin-modified alkyd.	Nitrocellulose lacquers, sanding sealers.	..
	Teglac, Z, 152.	Modified maleic type.	Pale interior oil varnishes of good colour retention.	..
	Teglac 161	" "		..

CHAPTER XII

PETROLEUM HYDROCARBON, OLEFINE, AND RUBBER RESINS

By R. S. MORRELL

PETROLEUM HYDROCARBON RESINS

PRODUCTS for which the petrol industry would be able to supply raw material are:

- (1) Natural petroleum resins from crude residua and heavy distillates obtained by light hydrocarbon precipitation, e.g. liquid propane.¹
- (2) Cracking products, e.g. cracking-coil tar-resins by condensation of highly condensed petroleum hydrocarbons (such as those which are present in the tar bottoms from cracking operations) with formaldehyde or ethylene chloride.
- (3) 'Santoesin', obtained by the polymerization of olefines and diolefines by means of aluminium chloride.²

F. W. Sullivan, V. Vorhees, A. W. Neeley, and R. V. Shankland have pointed out that olefines polymerize with $AlCl_3$ to form lubricating oils, but these oils are difficult to separate from the resins,³ so that it is advisable to have a proper ratio of olefines to diolefines and substituted aromatics; olefines and aromatics with $AlCl_3$ give substituted aromatics, e.g. amylene and toluene produce *p*-amyl toluene. If excess of olefines be present, di- and tri-substitution may take place. These polysubstituted products are, however, high-boiling oily compounds. It is difficult to determine the reactions taking place with a complex cracked distillate. In the presence of $AlCl_3$ the following reactions are believed to take place:

- (a) Reaction of olefines to form high-boiling oily polymers (lubricating oils).
 - (b) Reaction olefines with aromatics to form substituted aromatics.
 - (c) Polymerization of di-olefines and olefines to form resins (cf. p. 321).
 - (d) Reaction of di-olefines with substituted aromatics to form resins.
- (4) Polybutene products of the polymerization of unsaturated

gaseous hydrocarbons ranging from viscous oils to rubbery materials with mol. wts. up to 300,000:⁴

α -butylene (1-butene) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$;

$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$ (2-butene);

$(\text{CH}_3)_2\text{CH}=\text{CH}_2$ (isobutene, isobutylene);

butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$;

isoprene $\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{CH}=\text{CH}_2$.

In general the resins prepared *directly* from petrol fractions are poor in colour, and so far little success has been had in attempting to utilize them. Most crude oils contain resinous constituents, frequently referred to as complex hydrocarbons, probably polycyclic, frequently containing sulphur, and sometimes oxygen. Natural petroleum resins are in general dark coloured, fairly susceptible to oxidation, being converted to highly insoluble asphaltenes.

Resins may also be formed during the processing of the oil and by direct synthesis from them. New techniques of thermal cracking and catalytic processes are revolutionary. Cracking-coil tar-resins may be recovered by absorption, but it has been found preferable to subject the tar to distillation and solvent extraction. Treatment of the reduced tar with metallic halides is especially advantageous, both for increasing the yield and causing separation of undesirable constituents. Petroleum distillates, particularly those of high aromatic content, may be condensed with formaldehyde to form useful resins.

Less highly aromatic stocks may be practically converted to resinous material by chlorination followed by dehydrohalogenation either at elevated temperatures or with metallic halides. The above is a summary of a paper on the production of petroleum resins by S. C. Fulton and A. H. Gleason.⁵ The production of resins from the light petroleum aromatic distillates by treatment with formaldehyde will be discussed later; cf. p. 319.

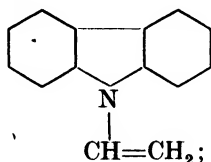
Resins from polybutenes (polybutylenes) (cf. Chapter XV, p. 421). Cracked petroleum contains considerable quantities of iso-

butylene $\left(\text{CH}_2=\underset{\text{CH}_3}{\text{C}}\right)$ which may be separated and polymerized

by metallic halides (Al, Sn), BF_3 to yield open-chain polymers with low mol. wts. Low-temperature polymerization by BF_3 seems to be the best method of obtaining polymers of high mol. wt., but the catalytic activity of AlCl_3 may be improved by the addition of anhydrous ferric chloride (B.P. 528,178). Promising results have been obtained by the use of Gustavson compounds as catalysts; these are double compounds of aluminium halides and aromatic hydrocarbons, e.g. butyl benzene and tripropyl benzene (B.P. 530,253). Polyisobutylenes as plastics are known as 'Vistanex'

(U.S.A.) and 'Opponals' (Germany). (Vistanex Polybutene LM is a colourless viscous liquid, mol. wt. 2,000–10,000. Vistanex Polybutene, MM and HM, mol. wt. 25,000–400,000, are tough elastic solids.)

The molecules of the polymeride (Oppanol) are considered from X-ray investigations to be chain-like and spiral and not zigzag like rubber molecules⁶ (cf. Appendix I, Chap. IV). One of the defects of the polyisobutylene polymerides is poor heat stability, but this has been improved by adding small quantities of phenols and mercaptans.⁷ Interpolymerides have been prepared, notably with fumaric esters and N-vinyl carbazole

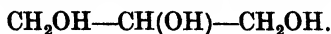


the latter polymeride shows a reduced tendency to *cold flow*.⁸ They range from viscous fluids to tough rubbery solids of rubber consistency with mol. wt. 100,000 and are used for electrical and other applications.⁹ They are thermoplastic with elasticity up to 100 per cent. when stretched, and returning to 5 per cent. when released. They are impervious to water, resist acids and alkalis, but are attacked by halogens; they are stable to oxygen and ozone. Differences between polybutenes and natural rubber show that outright replacement of natural rubber is not permissible for many applications (S. Longman, 1940). Polyisobutenes (polyisobutylene) occupy a position between the thermoplastics of the vinyl family and the synthetic rubbers of the butadiene type. Generally all these products are known as polybutenes, although derived essentially from isobutene containing varying percentages of the *n*-butenes.

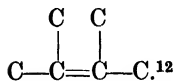
The uses of polybutenes are:

- (1) Incorporation with rubber to improve resistance to zone and corrosive chemicals.
- (2) Blending with motor oils to improve viscosity (Exanol).
- (3) In greases and special lubricants to replace rubber additions and to impart stringiness.
- (4) Blending with asphalts to improve their weathering.
- (5) Blending with paraffin wax to increase the viscosity and to prevent the tendency of wax to penetrate a surface to which it is applied. The addition of polybutenes of more than 10,000 mol. wt. produces bonds of considerable strength after heat-sealing; straight wax has little or no bond strength.¹⁰

The conversion of propylene (in cracked gases from petroleum refineries) into glycerol is attracting attention on a commercial scale in U.S.A. Propylene ($\text{CH}_2=\text{CH}\cdot\text{CH}_3$) is converted into allyl chloride ($\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$), which is hydrolysed to glycerol:—



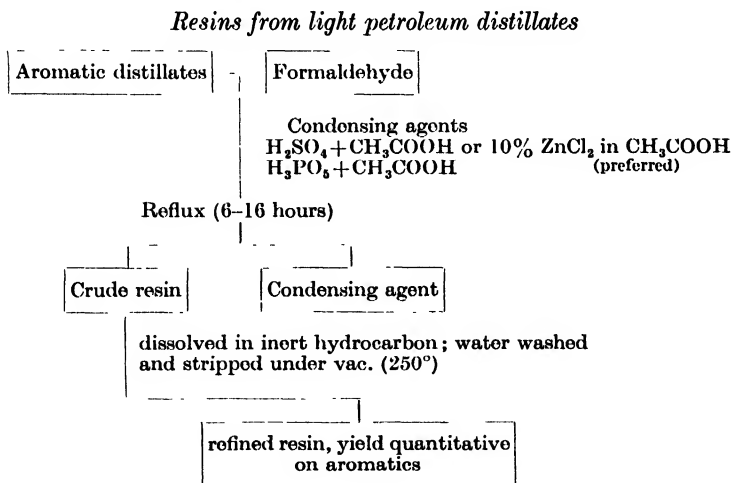
Propylene may be catalysed by Gayer's silica at 350° to give 2-methyl-2-pentene $\left[\begin{array}{c} \text{C}-\text{C}-\text{C}=\text{C}-\text{C} \\ | \\ \text{C} \end{array} \right]$ and 2, 3-dimethyl-2-butene



Another interesting example is furnished by a patent specification by W. B. Borst and J. C. Morrell claiming the production of a gummy material, which with fillers gives good moulding with insulating properties and chemical resistance; the source is a cracked petroleum distillate of the b.p. range of gasoline which is oxidized by oxygen at 125° in the presence of a metallic oxide (Fe, Co, Ni, Cr and Mn).¹³

ALDEHYDE PETROLEUM AROMATIC RESINS

The resins formed during the cracking of petroleum oils (cf. p. 317) are inferior to those synthesized from various distillates.¹⁴ Resins may be more advantageously obtained from petrol aromatic distillates with sulphur dioxide, phenol, &c., resulting in the concentration of highly aromatic compounds which may be condensed with para-formaldehyde to give useful resins. This reaction, due to Nastyukov,¹⁵ gives rise to Neoformalite resins. The scheme below shows the stages of the process.¹⁶



The resins obtained are yellow to amber in colour (K-X rosin scale), m.p. up to 140°, mol. wt. > 700, non-heat hardening and non-reactive; they are very soluble resins generally, but are not soluble in the lower alcohols or light petroleum; with drying-oils they are compatible giving alkali-resistant films, but not specially

resistant to hot and cold water; they are adhesive, of intermediate gloss, yellowing slightly with age. Another source of suitable aromatic components is to be found in the refining products of lubricating oil, which can be separated by extraction with phenol, nitrobenzene, &c. The resins are reddish to amber in colour.

According to A. E. Dunstan¹⁷ the petroleum industry will furnish the starting-out materials for a whole range of products, so diverse as ethylene glycol (the anti-freeze in the motor-car); sulphur, from the crude gases at the oilfields; synthetic motor fuel, prepared from methane oxidized into a liquid fuel; the isomerization of normal paraffins; explosives, e.g. T.N.T. (for the production of high-grade toluol from petroleum reference may be made to the *Chemical Age*, 1940, p. 121); synthetic rubber, by the intensive polymerization of ethylene; high polymers of value in increasing the viscosity of lubricants; a whole range of derivatives of the aromatic hydrocarbons obtained by pyrolysis or by the cyclization and aromatization of straight-chain paraffins; resins and plastics from the polymerization products of olefines, e.g. isobutene (isobutylene); acetylene by the dehydrogenation of methane; ethers and ketones as solvents and high anti-knock fuels; alcohols, esters, and a whole range of solvents through the halogen derivatives of paraffins; the very striking synthesis of glycerol from propylene. The new industry, based on petroleum, is certain to outstrip the coal-tar industry in magnitude of its operation and the variety of the products. The mechanism of the polymerization of petroleum and other hydrocarbons will be discussed in Chapter XV (The Problems of Resinification).

POLYETHENES

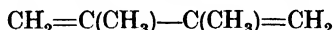
If ethylene (or propylene) free from oxygen or sulphur be polymerized in the presence of aluminium chloride in an apparatus ensuring non-contamination with iron, polymers can be isolated as viscous liquids of value as aircraft engine lubricants.¹⁸ Aluminium fluoride also catalyses the polymerization of olefines (as well as of diolefines to yield liquid products). Olefine interpolymerides with diolefines and fibrous materials in the presence of sulphur and metallic halides can be heated in a mould at about 180° to give resin substances.¹⁹

Although the polymerization of ethylene to liquids and sticky gums has been known for a long time, the production of solid and flexible polymerides was accomplished on an industrial scale by the Imperial Chemical, Industries, Ltd., whereby the gas, mixed with a small proportion of oxygen was subjected to a pressure of 1,200 atmospheres, precautions being taken to prevent the temperature reaching the point of explosive decomposition. Films, coatings, tapes, &c., can be made from the polymeride (mol. wt. above 6,000) by heating it above the softening temperature (110°) and rapidly cooling. The threads obtained by extruding the molten polymeride (mol. wt. above 6,000) or its hot solution in an organic solvent can

be improved mechanically by cold stretching operation at rather lower pressures to produce semi-solids or greases. Halogen derivatives of the polymers (mol. wt. 2,000-400), obtained by halogenating in a molten condition or in an inert solvent, vary with the percentage of chlorine from rubbery to horn-like materials, some of which find use in electrical insulation.²⁰ Compounds of high molecular weight have been obtained by the removal wholly or in part of the halogen from the corresponding halogenated derivatives, and interpolymerides of ethylene with one or more organic compounds capable of forming higher polymerides have been described. The usual high-pressure technique is used. Most of these interpolymerides (co-polymerides) are soft solids, but a few with styrene and dimethacrylate are hard²¹ (cf. Chapter V, p. 190).

CO-POLYMERIZATION PRODUCTS OF OLEFINES AND DIENES

Detailed accounts of the nature and properties of Buna and other synthetic rubbers have appeared in the specialist press of the rubber industry, and as to the chemical characteristics of the synthetic polymers involved reference may be made to papers presented by P. K. Frohlich of the Standard Oil Development Co., U.S.A., to the New York Group of the American Chemical Society (1940), and H. Barron.²² Rubber has certain shortcomings that limit its application. Its peculiar molecular structure accounts for its elastic properties and mechanical strength, but its weak points are its pronounced chemical reactivity, lack of heat stability, and susceptibility to acids. From a structural standpoint the rubber molecule may be considered as a polymer of isoprene (2-methyl-butadiene). The original methyl rubber was made from 2,3-dimethyl butadiene



because this di-olefine could be made available more readily than isoprene. The present effort is to reproduce, or even improve upon, the structural characteristics of the rubber molecule. As shown below, the conditions of polymerization (especially emulsion polymerization of butadiene; cf. p. 371) and the formation of co-polymers, also under emulsion conditions, have a pronounced effect on the physical and chemical properties of the resulting polymer.

Co-polymerization has made synthetic rubbers into potentially commercial materials. By varying the nature and amount of the plastic used synthetic rubbers with specialized properties may be produced. The use of oil wastes (cf. p. 322) as a raw material to supply butadiene at a low cost is a progressive step. The price of commercial synthetic rubber may in a few years fall to 1s. per lb. (Barron). It is stated (*Chemical Age*, 1941, p. 147) that yields of 20-30 per cent. of butadiene can be obtained from the dehydrogenation of butylene at 600-650° by vanadium oxides or chromium-molybdenum mixtures as catalysts. In B.P. 532,942 a process is described whereby high-yield conversion of α -butylene diluted with

carbon dioxide (1:1) is effected at 575° with a bentonite layer containing 5 per cent. nickel.

In the polymerization of butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) to give Buna (a straight butadiene polymer) the process can be conducted to yield products ranging from oils to hard, horny solids; reference may be made to Nauntons' *Synthetic Rubber*, 1937, for details of Buna and its varieties. One of the best catalysts in this connexion is an anhydrous halogen halide. Preliminary low-temperature polymerization (at -20°) of the liquid butadiene in the presence of an anhydrous hydrogen halide is recommended to give drying-oil substitutes.²³ This step is followed by separation of a more volatile fraction and further polymerization of the residue. The aluminium fluoride catalyst mentioned above has been used in the vapour-phase polymerization of butadiene to give pale-coloured oils boiling not above 200° (cf. Chapter XV, p. 423, 'The Problems of Resinification').

Co-polymerization Products.

Improved products resulting from polymerization of mixtures of olefines and dienes may cause the superseding of butadiene by copolymers of butadiene and styrene (Buna S) or butadiene and acrylonitrile (Perbunan, Buna N, Perbunan N, Hycar); both styrene and acrylonitrile contain olefinic bonds. When a mixture of buta-

Established Synthetic Rubbers (Barron, loc. cit.)

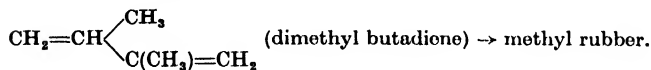
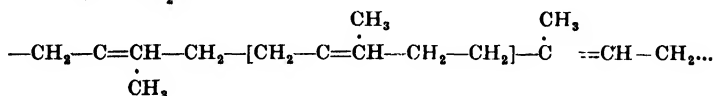
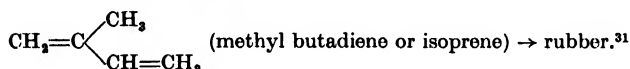
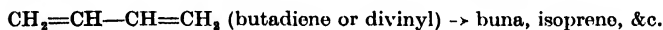
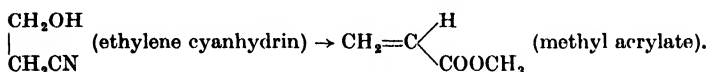
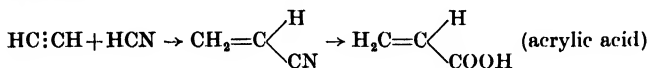
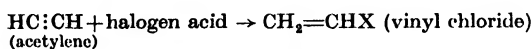
<i>Synthetic rubber</i>	<i>Manufacturer</i>	<i>Date available</i>	<i>Composition: Polymers of</i>	<i>Raw materials</i>
Neoprene	Du Pont de Nemours & Co.	1931	Chloroprene	Carbide
Thiokol	Dows	1931	Ethylene polysulphide	..
Perduren	I.G.	1935	" "	..
Buna 85	I.G.	1935	Butadiene "	Carbide
Buna S.	I.G.	1935	Butadiene and styrene	Carbide and coal
Perbunan	I.G.	1936	Butadiene and acrylic nitrile	" "
Hycar	B. F. Goodrich, Phillips Oil Corp. } Goodyear	1940	Butadiene and acrylics	Oil wastes and coal
Chemigum		1940	" "	Oil wastes (a great advance)
Butyl	Standard Oil Development	1940	Olefines and diolefines	Oil wastes
Buna	Standard Oil of N.J. } Firestone	1940	" "	Oil wastes and coal
Vinylite		Union Carbide and Carbon Corp.	1930	Vinyl chloride
Koroseal	B. F. Goodrich	1934	" "	"
Mipolam	I.G.	1935	" "	"

diene and ethylene is polymerized by high pressure and high temperature (cf. B.P. 471,590) a soft rubbery solid is obtained; under similar conditions a mixture of ethylene and styrene yields products of varying degrees of toughness, according to the proportions of the ingredients; a soft wax melting at 60° is derived from a mixture of ethylene and limonene.²¹ On the other hand, using a catalyst of BF_3 type and operating at about ordinary temperatures and pressures, Du Pont de Nemours & Co.²⁴ have produced liquid polymers from olefine-di-olefine mixtures. An oil with lubricating properties may be prepared from *n*-octene-1 and butadiene; drying-oils and varnishes from mixtures of butylene and chlorbutadiene or from butylene, isobutylene, and butadiene. The Standard Oil Development Co. have obtained a butyl rubber by co-polymerization of an olefine (butylene or isobutylene) and a small proportion of a diene, which after vulcanization is virtually completely saturated as to its molecules, and so is exceptionally resistant to chemical agents.²⁵

Sulphur dioxide olefine resins. Many olefines react with liquid sulphur dioxide to yield heteropolymer products that give coherent mouldings comparable in mechanical and electrical properties to some commercial plastics. The sulphur dioxide olefine products are thermo-plastic. The ethylene compound has a high softening temperature and is insoluble, whereas the 1-decene substance is rubbery and soluble in organic solvents. Propylene resin has a moulding temperature 180–200°; *n*-butene resins have 125–80°. Resins from 2-olefines have higher softening-points, are less soluble, and are more resistant to alkalis. R. D. Snow and F. E. Frey, experimenting with ethylene, propene, 1-butene, 1-pentene, and isopropylethylene, state that the reaction takes place only in the presence of catalysts (mild oxidizing agents, e.g. nitrates), or when the reactants are irradiated with light of less than 3,000 Å; in addition there exists a temperature characteristic above which no reaction takes place.²⁶ Recent patents of interest are (1) the removal of tertiary olefines from mixtures of olefines by polymerization before treatment with sulphur dioxide,²⁷ (2) by the use of silver sulphate, silver sulphite, or nitrate as catalysts,²⁸ and (3) Du Pont de Nemours & Co. describe the formation of olefine- SO_2 polysulphones, e.g. $\text{CH}_2:\text{CHCH}_3$, $\text{CH}_2:\text{CHMe}\cdot\text{CO}_2\text{Me}$, with SO_2 with benzoyl peroxide and ascaridole as catalysts at -80° , allowed to reach room temperature in 3 hours, after 7 days. The polymer contains 22 per cent. S.²⁸ A colourless transparent moulding is produced at 160–5/ ~ 670 atm. C. S. Marvel and W. H. Sharkey have shown that the polysulphones obtained by using peroxide catalysts may be identical with those prepared under the influence of ultra-violet light.²⁹ C. S. Marvel and F. L. Glavia have also investigated the vinyl halide polysulphones. They characterize the products made by using peracetic acid and show that they differ from those made with ascaridole as catalyst.³⁰ Vinyl bromide gives similar products. For the function of the catalysts cf. Chapter XV, p. 423.

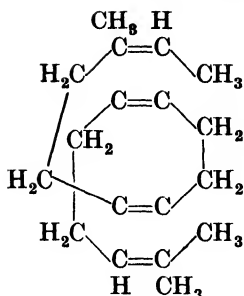
RESINS FROM RUBBER AND ITS DERIVATIVES

It is again advisable to discuss here the resemblances of the new synthetic resins to rubber. Elasticity is the outstanding property of rubber, whilst its disadvantages are lack of resistance to oil and solvents, its inflammability, and its tendency to take up water and so affecting its electrical properties, lack of resistance to sunlight and oxygen, susceptibility to ozone, and the influence of metals. Comparison may be made with polystyrene, polyvinyl, polyacrylic, and polymethacrylic resins. Polystyrenes at 100° are elastic and rubbery; polymethacrylic approach glass and rubber, and neoprene most closely resembles it:

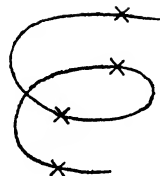


Plastic and synthetic rubber monomers all have a common $\text{CH}_2=\text{C}$, the latter also having a conjugated double bond, which confers elasticity and ability to form bridges between the long-chain molecules with the production of thermo-setting or vulcanizable materials.³²

Naunton has pointed out that the elasticity is definitely associated with its structure.³³ Alteration of structure causes the elasticity to disappear and the resulting substance is thermoplastic. An interesting formula for rubber is given by Kirchhof where a spiral arrangement is given to explain the elastic properties.³⁴ For fuller information respecting the properties of rubber reference may be made to Naunton's book, and to Appendix I, Chapter XV, for the special formula of butadiene polymers.



Crude rubber molecule



Double linkages, x

Bruson has developed commercial plastics by the action of chlorostannic acid on rubber either directly in the mill or in benzene solution.³⁵ The products are thermoplastic and have good resistance to water with exceptional electric properties. Bruson, Sebrell, and Calvert have obtained coloured products by the action of metallic halides on rubber in benzene solution, which are decomposed by alcohol yielding thermoplastic conversion products in many respects similar to the thermoprenes, being isomeric with rubber and being less unsaturated.³⁶ Winkelmann and Jones³⁷ by milling rubber with 10 per cent. ferric chloride at 100° for 15 hours obtained a hard brittle thermoplastic resin.

The use of rubber in paint vehicles has been discussed by H. P. Stevens and N. Heaton.³⁸ Rubber may be incorporated into a paint vehicle, because its viscosity may be rapidly reduced by melting with a drier such as, and especially, cobalt linoleate, the best proportion being 2½ per cent. of the rubber. Under these circumstances flat paints, ready-mixed gloss paints, and enamels with good flow-properties and elasticity may be prepared. The addition of rubber to various proprietary brands of gloss paint showed that a proportion in the order of 4 per cent. is sufficient to eliminate brush marks and produce almost an enamel gloss. Whilst there is no improvement in durability, the addition of rubber does not in any way impair its resistance to decay. The use of bronze powders with rubber linseed-oil vehicles is satisfactory. A distemper based on rubber latex can be rendered stable enough to be brushed, but it is almost impossible to clean the brush. I. T. Gurman³⁹ has described the properties and uses of Balata and gutta-percha resins.

It has been found that catalytically oxidized rubber, made by aerating a solution of rubber in white spirit containing cobalt linoleate, may prove a useful material for resin-bonded mouldings, electrical insulating varnishes, paints, and lacquers. It has been shown by Stevens and associates⁴⁰ that, by catalytic oxidation of rubber solutions of greatly reduced viscosity (see *ante*), such solutions have desirable effects when incorporated in paints and varnishes. A further study of this catalytic oxidation has resulted in the production of resins of interesting properties⁴¹ which have been named

Rubbones; Rubbone 'B' ($C_{10}H_{16}O$) is useful for electrical insulation because it may be rendered fluid by heat and thermo-hardened on stoving. Rubbone can be vulcanized by sulphur or sulphur chloride in the normal way to give ebonite-like products. Cold-cured or halogenated films are elastic and perfectly clear; they do not absorb moisture and are impermeable to gases (in contra-distinction to vulcanized rubber).

Depolymerized rubber. In order to utilize rubber in the coating industry efforts have been made to reduce the degree of polymerization. In 1910 Harries⁴² produced his iso-rubbers, which are less saturated than raw rubber. Kirchhof⁴³ and Fisher⁴⁴ found that treatment of rubber on the mill with sulphuric acid or sulphonic acids (chlorosulphonic acid) and sulphonylchlorides gave tough thermoplastic materials resembling gutta-percha, balata, and even shellac; these are the *thermoprenes* which have found some application for moulding, but are mainly employed in solution for sticking rubber to metals, being the basis of the 'vulcalock' process. They can be vulcanized by sulphur. All are hydrocarbons with the same composition as rubber, but with fewer double bonds; this has been attributed by Ostromisslenski, Fisher, Kirchhof, and Staudinger to cyclization within the rubber molecules.⁴⁵

CHLORINATED RUBBER VARNISHES

Chlorine may be passed into a solution of raw rubber in benzene at 80°, or light crêpe rubber may be saturated with the gas. The product is soluble in benzene and common solvents and is stable up to 150–70°. The films are non-inflammable and not easily disintegrated by chemicals; brittleness is reducible by plasticizers (tri-cresyl phosphate). The resin has been recommended as varnish for aircraft and automobiles, also as a layer between cement and as an anti-rust composition.⁴⁶ Alexander Parkes in 1846 and S. J. Peachey in 1915 took out patents for the manufacture of these products. A process developed at Tornesch first made possible the large-scale production of a stable chlorinated rubber. The product 'Tornesite' is a yellowish-white powder containing 67–69 per cent. of chlorine. It is stable, chemically inert, non-inflammable, non-combustible, and practically odourless. Its specific gravity is 1.5 and its bulking value is 0.08 gal. per lb., the same as that of nitrocellulose. It possesses great resistance to acids, alkalis, and salts, and strong adhesion to metal and concrete, without sacrificing hardness. In the opinion of R. A. Coolahan⁴⁷ Tornesite appears to be the most outstanding protective coating which he has tested. Unpigmented Tornesite films, like clear nitrocellulose lacquers, break down under direct outdoor conditions, but are more resistant when pigmented, and paints made with a variety of pigments show excellent protection for metal; moreover, the films can be polished to a good surface. A film formed from a simple solution of Tornesite is very resistant to chemical action, but has poor adhesion, which is much improved

by plasticizers, especially Herculyn (hydrogenated methyl abietate). The most economical and suitable plasticizers are drying-oils, e.g. bodied wood-oil and blown linseed oil.⁴⁸ The varnishes containing drying-oils and aromatic thinners can replace nitrocellulose lacquers. In a paint the Tornesite is dissolved in a 2:1 mixture of high-flash naphtha and xylol to give a 30 per cent. strength. The acid resistance of the paints is said to be excellent, and when properly compounded can be made to adhere perfectly to cement or metal, so that it is most valuable for tank paints. It is as good as Seal Paint (cyclo-rubber), superior to Dualprene, which owing to its lack of stability loses hydrochloric acid. Plyaform is not in the same class as Tornesite because it is only chlorinated to the extent of 1.7-2 per cent.⁴⁶

During the last few years considerable attention has been paid to their development. In an Annual Report of the Chemistry Research Board it is stated that hard boards of impregnated linen or very light laminated materials can be obtained according to the temperature and pressure conditions.⁴⁹ Chlorinated rubber can be used with fillers as a moulding material or can be used alone as a plastic. Transparent mouldings under a pressure of 1 ton per sq. in. can be obtained by suitably controlling the temperature between 120° and 70°. It unites with basic colouring matters (carbinol base of rosaniline or of brilliant green) to give coloured films.

Redfarn and Schidrowitz have developed a process whereby suitably plasticized chlorinated rubber may be expanded to yield a porous sponge, e.g. *alloprene* moistened with alcohol may be extruded through a small orifice under pressure. They also describe mechanical modifications necessary to the type of extruding machines in the production of rods and tubes from rubber, casein, and cellulose acetates for the production of expanded chlorinated rubber by extrusion. The material is cellular-like, of low density, non-inflammable, and possesses excellent heat-insulation properties.⁵⁰ J. P. Baxter and J. G. Moore have given a full summary of the uses of chlorinated rubber with special attention to *alloprene* to which brief reference may be made. The development of the chlorinated rubbers in their use in the preparation of paints and lacquers, moulding powders, floor covering, pipe-joints, &c., has become very marked. High-grade uniform and stable chlorinated rubber is now available commercially and a considerable number of applications of this substance have been discovered and are now being developed. Baxter and Moore⁵¹ point out that the stability of chlorinated rubber depends on three factors: (1) Free hydrochloric acid; there should be no free acidity in the sample. (2) Photochemical instability, due to liberation of HCl; the method of protection as in a paint is to use a pigment, e.g. TiO₂, Fe oxide, capable of absorbing and reflecting the harmful radiation or to add to the chlorinated rubber an ultra-violet filter of the dibutyl-phthalate type. (3) Thermo-instability; the higher the degree of chlorination the greater the heat stability. A properly prepared chlorinated rubber is stable up to 130°. Stabilizers are not

recommended, although ethylene oxide derivatives have been proposed.⁵² The plasticizers recommended are Herculyn, chlorinated drying-oils (Dunlop Rubber Co.)⁵³, and Cereclor (I.C.I.), a viscous yellow liquid. Its resistance to moisture is very marked. They have also described how dark brown semi-translucent mouldings may be obtained under 3-6 tons pressure at 135-40°. By suitably compounding with chlorinated waxes, useful plastics are obtained suitable for tank linings, pipe jointings, &c. In 1923 N. McGavack showed that when chlorine gas was passed into a benzene solution of rubber at the ordinary temperature a transparent film could be obtained, which was placed on the market as transparent moisture-proof paper.⁵⁴ The Marbo Products Corporation improve the transparency by working at -10° to -35°.⁵⁵

Resistance to alkalis, salts, and weathering of compositions of chlorinated rubber in solution may be increased by the incorporation of a thionated product of *p*-alkyl substituted anilines, for example those formed by the action of sulphur on *p*-toluidine.⁵⁶ Improved mechanical and chemical resistance can also be obtained by incorporating as a hardening agent a small amount of a :C:X compound, where X is S, NH, or NR, and heating to 80-150° when solid; an example is thiobenzthiazole.⁵⁷ Fire-resisting compositions may be prepared from chlorinated rubber, drying-oils, white lead, and whiting. O. Jordan⁵⁸ points out that chlorinated rubber paints do not adhere to concrete or cement, especially if they be damp, but by the addition of Plastomoll (polyvinyl resins) paints are protected from water and adhere well.⁵⁹ A plasticizer wax and an oil-modified alkyl resin may be incorporated with fully chlorinated rubber; the products are suitable as moisture-proofing compositions for paper, &c.⁶⁰ Carleton Ellis⁶¹ incorporates a plasticizer formed by heating an oil-soluble phenol resin and tung or castor oil at 240°.⁶²

Duroprene (United Alkali Company). Chlorinated rubber ($(C_{10}H_{13}Cl_7)_n$ or $C_{10}H_{15}Cl_7$) is soluble in aromatic and chlorinated hydrocarbons, insoluble in aliphatic hydrocarbons, alcohol, and ethers; 10 per cent. solution in benzene and solvent naphtha is used as a varnish. It is unacted on by alkalis and acids, alcohol, ether petrol, and paraffin oils.⁶³

Tegofan. Chlorinated rubber (neutral) decomposes without melting on heating; soluble in aromatic and chlorinated hydrocarbons, tetralin, drying-oils, but insoluble in alcohol, glycerol, and aliphatic hydrocarbons (Chemische Fabrik Buckau). It gives chemical-resistant and waterproof coatings.⁶⁴

Pergut. A chlorinated rubber resin manufactured by the I.G. Farbenindustrie, A.-G.

Detel. A chlorinated rubber resin manufactured by the Detel Products (U.S.A.).

Dartex. A chlorinated rubber resin manufactured by the Metallgesellschaft, A.-G.; *Proten*, by the Soc. Elettrica ed Elettrochimica di Caffaio, Italy; and *Aizen*, by the Nippon Soda K.K., Japan.

Ebonite.

Description of the chemistry and technology of ebonite belongs to a treatise on rubber and will only be referred to very briefly here.

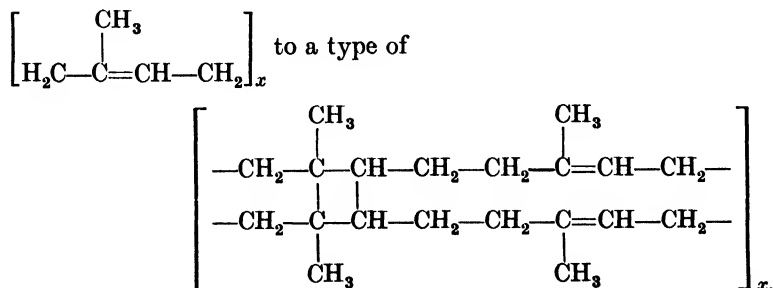
Ebonite is the product of the vulcanization of rubber with 25–32 per cent. sulphur at 130–60°. The addition of 2–5 per cent. selenium accelerates the curing and improves the product. It is one of the best commercial dielectrics. For tables giving the numerical values of the physical constants, reference may be made to *British Plastics*, 1938, 10, 280, to H. F. Church and H. A. Daynes,⁶⁵ and to Davis and Blake on the Chemistry and Technology of Rubber.

CYCLIZED RUBBERS

Pliolite (Plioform).⁶⁶ Obtained by heat treatment of rubber in a solvent with stannic chloride or chloro-stannic acid pliolite is suitable as a thermoplastic for moulding and in solution in hydrocarbons for impregnation of fabrics, also for rods and tubes (Good-year Co.). Chemically the reaction product analyses about 96 per cent. $(C_5H^8)_x$ and a whole family of resins can be produced depending on the conditions of treatment. The group of materials prepared by this method has been named *Pliolite*.

The resins (s.g. 1.06; rubber is 0.93) are neutral, soluble in turpentine and aromatics, but not in alcohol or lacquer solvents; suitable for anti-corrosive coatings. Their physical properties vary from rubbery to hard shellac types. Pliolite powder is a fine white material.

When rubber is cyclized in solution with agents such as stannic chloride or chlorostannic acid there is at first an increase in viscosity followed by a gradual decrease, until a stage is reached where further heating produces no further reduction in viscosity. The longer the reaction is allowed to run, the harder and more brittle is the resulting resin. In the cyclization process the unsaturation of the original rubber is reduced to a half or a change from the conventional



H. R. Thies⁶⁷ has discussed the properties of mixtures of pliolite and rubber, where pliolite functions as a stiffening and hardening agent for rubber in the field of coated fabrics and of wire insulation; the pliolite content may vary between 10 and 25 per cent.

REFERENCES

1. P. T. Graff and H. O. Forrest, *Ind. Eng. Chem.*, 1940, **32**, 294.
2. C. A. Thomas and W. A. Carmody, *Ind. Eng. Chem.*, 1932, **24**, 1125; I.G. FarbenInd. A.-G., B.P. 413,007; B., 1934, 849; H. L. Waterman, *Chem. Weekblad.*, 1935, **32**, 342; B., 1935, 735; P. K. Frohlich, *Ind. Eng. Chem.*, 1940, **32**, 293.
3. F. W. Sullivan, V. Vorhees, A. W. Neeley, and R. V. Shankland, *Ind. Eng. Chem.*, 1931, **23**, 604.
4. P. K. Frohlich, loc. cit.
5. *Ind. Eng. Chem.*, 1940, **32**, 304.
6. R. Brill and F. Halle, *Naturwiss.*, 1938, **26**, 12; B., 1938, 413.
7. Standard Oil Development Co., B.P. 498,966; B., 1939, 123.
8. I.G. FarbenInd., B.P. 501,869; B., 1939, 465; and I.G. FarbenInd., B.P. 506,926; B., 1939, 861.
9. W. A. Gibbons, *Ind. Eng. Chem.*, 1939, **31**, 1199
10. R. M. Thomas, J. C. Zimmer, L. B. Turner, R. Rosen, and P. K. Frohlich, *Ind. Eng. Chem.*, 1940, **32**, 299.
11. E. C. Williams, *Ind. Eng. Chem. (News Ed)*, 1938, **16**, 630, and H. Barron, *Chem. Age*, 1939, **41**, 5.
12. F. C. Whitmore and R. F. Marschner, *Trans. Faraday Soc.*, 1936, **32**, 232.
13. U.S.P. 2,066,090 and 2,066,120; B., 1939, 404.
14. S. C. Fulton and H. G. Gleaves, *Ind. Eng. Chem.*, 1940, **32**, 304.
15. *J.S.C.I.*, 1904, **86** (1), 801; B.P. 289,920; *Cony. Theor. et. Appl. Chem.*, 1932, **2**, Abt. 1; B., 1938, 684.
16. S. C. Fulton, U.S.P. 2,035,123; B., 1937, 263.
17. *Nature*, 1940, **146**, 185.
18. I.G. FarbenInd. A.-G., B.P. 497,541; B., 1939, 125.
19. *Ibid.*, U.S.P. 2,195,747.
20. B.P. 471,590; B., 1937, 1309; B.P. 474,426; B., 1938, 942; B.P. 472,051; B., 1938, 635; B.P. 481,515; B., 1938, 625.
21. I.C.I., B.P. 497,643; B., 1939, 240.
22. *Chemical Age*, 1941, 107.
23. I.G., B.P. 500,769; B., 1939, 464.
24. B.P. 516,931; B. 1940, 265.
25. L. Light, *Chemical Age*, 1940, **43**, 240.
26. *Ind. Eng. Chem.*, 1938, **30**, 176.
27. Phillips Petroleum Co., B.P. 480,777; B., 1938, 1330.
28. *Ibid.*, U.S.P. 2,128,932; Du Pont de Nemours & Co., B.P. 528,051 (1939).
29. *J. Amer. Chem. Soc.*, 1939, **61**, 1603.
30. *Ibid.*, 1938, **60**, 2622.
31. H. Staudinger, *Die Hochmolekularen Organischen Verbindungen*, 1932, 378.
32. H. Barron, *Chem. Ind.*, 1938, 654.
33. *Synthetic Rubber*, 1937.
34. *Kautschuk*, 1930, **6**, 31.
35. *Brit. Plastics*, 1938, **10**, 16.
36. *Ibid.*
37. *Rubber Age*, 1927, **21**, 502.
38. *J. Oil Col. Chem. Assoc.*, 1934, **17**, 8.
39. *India Rubber World*, 1933, **88**, 31; *Chem. Zentr.*, 1934, **105** (1), 1400
40. *Bulletin, Rubber Growers' Assoc.*, 1933, **15**, 600; B.P. 407,038 (1934); and *J.S.C.I.*, 1938, **57**, 128 T.
41. B.P. 417,192.
42. *Untersuchungen*, Leipzig, 1919, p. 203.
43. *Kautschuk*, 1928, **4**, 142.
44. *Ind. Eng. Chem.*, 1927, **19**, 1325.
45. *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1928.
46. R. Salzer, *Farbe u. Lack*, 1932, 452; K. Kojima and Y. Toyabe, *J.S.C.I. Japan*, 1933, **36**, 236; B., 1933, 757.
47. *Chem. Ind.*, 1934, 630; B.P. 405,699 (1935); B.P. 427,810 (1935); B.P. 427,727 (1935).
48. F. Rosendahl, *Chem.-Ztg.*, 1932, **56**, 729.
49. *Chem. Ind.*, 1938, 936.
50. Conference on Rubber Technology, 1938; *Brit. Plastics*, 1938, **10**, 16.
51. *J.S.C.I.*, 1938, **51**, 327 T.
52. B.P. 418,230; B., 1935, 13.
53. B.P. 420,116; B., 1935, 114.
54. *Ind. Eng. Chem.*, 1923, **15**, 961.
55. U.S.P. 2,047,987; B., 1937, 1370; U.S.P. 2,046,986; B., 1937, 816.
56. J. R. Gelgy, A.-G., B.P. 498,989; B., 1939, 637.
57. Raolin Corp., B.P. 491,141; B., 1939, 183.
58. Br. Insulated Cables Ltd., B.P. 498,181; B., 1939, 598.
59. *J. Oil Col. Chem. Assoc.*, 1939, **23**, 208.
60. J. G. Moore, E. Moores, and I.C.I., B.P. 488,937; B., 1939, 179.
61. U.S.P. 2,072,069; B., 1939, 179.
62. M. Loops, *Farben-Chem.*, 1938, 414; B., 1939, 174.
63. A. Lambie, *Oil and Col. Trades J.*, 27 May 1920; Peachy, B.P. 1,844 (1915).
64. B.P. 416, 252; B., 1934, 1023.
65. *J. Rubber Res.*, 1937-9; B., 1937, 1378; B., 1938, 697; B., 1939, 754.
66. H. R. Thies and A. M. Clifford, *Ind. Eng. Chem.*, 1934, **26**, 123; H. A. Bruson, L. B. Sebrell, and W. C. Calvert, *Ind. Eng. Chem.*, 1927, **19**, 1033; Goodyear Tyre Co., U.S.P. 1,846,247; B., 1932, 1093.
67. H. R. Thies, *Ind. Eng. Chem.*, 1941, **33**, 389.

CHAPTER XIII
MISCELLANEOUS RESINS

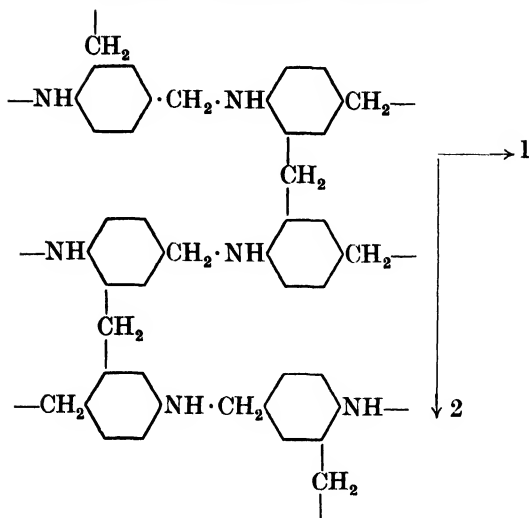
By R. S. MORRELL

ARYLAMINE ALDEHYDE RESINS

AMINES, it is well known, can be condensed with aldehydes. Benzaldehyde and dimethyl-aniline, for instance, give tetra-methyl-diamino-triphenyl-methane, the leuco-base of the dyestuff malachite green. A resin, however, is obtained from aniline and formaldehyde, in equimolecular proportions, in the presence of a small quantity of acid or alkali. At first anhydro-formaldehyde aniline (methylene-aniline) is formed. With an alkaline catalyst methylene-diphenyl-di-imide, $C_6H_5NH-CH_2-NHC_6H_5$, is produced, and is converted on heating into highly polymerized forms which are of a resinous nature. When either of the above substances is heated with aniline and aniline hydrochloride for 12 hours a conversion ensues to a mixture of 90 per cent. 4-4'-diamino-diphenyl-methane and 10 per cent. 2-4'-diamino-compound. The formation of *p*-amino-benzyl-aniline as an intermediate product has been protected by patent rights. On oxidizing the first diamino-compound dyes are formed; and by the use of ortho- or para-toluidine or dimethyl-aniline in place of aniline there are similar condensations and further dyestuffs are produced. All these reactions indicate the manner in which condensations to form resins may take place; also when formaldehyde condenses with diamines, with phenyl-hydroxylamine, benzylaniline, and carbazole, by variation in the conditions resins are alternative products in many cases.

The aniline-formaldehyde resins are thermoplastic and do not soften appreciably below 150° and can be employed at higher temperatures than the average thermoplastic materials. They can also be moulded without fillers to give brown translucent objects of considerable mechanical strength. The complex condensation reaction between aniline and formaldehyde has been investigated by K. Frey and collaborators,¹ who discuss the production of Schiff's bases (methylene di-imides) (e.g. $NH_2C_6H_5 + CH_2O \rightarrow [C_6H_5N=CH_2]$) under neutral, alkaline, and acid conditions. Houwink (loc. cit.) states that from a physical aspect these resins possess peculiar properties. They show no hardenable tendency, and Frey (loc. cit.) considers the structure on p. 332 as possible. This is not thermo-setting in the sense of a phenol-formaldehyde resin, so that long chains in the direction of arrow No. 1 rather than arrow No. 2 could be formed.

A. Bytebier² claims to have been the first to have prepared the above compounds in an attempt to purify diamino-diphenyl-methane from the oily products formed during the action of formaldehyde on



aniline in the presence of acids. On subjecting the reaction mixture to many hours' heating *in vacuo* the diamino-diphenyl-methane is distilled off, leaving behind a hard plastic mass soluble in varnish solvents and capable of being moulded. No mention is made of the production of an infusible form.

Aniline and formaldehyde, in the proportions given above, furnish a light-coloured resin softening at 70° , but not polymerized by heat to an infusible form. The resin is soluble only in acetone and β -chlorotoluene. Methylene-aniline (anhydro-formaldehyde-aniline) may be used as the starting-point in the preparation of aniline resins. When heated at 130° for a long time it is converted into a resin easily soluble in benzene and miscible with oils, fats, &c. The product has been recommended for use in augmenting the solubility of natural or synthetic resins which are not completely soluble, and it can be used as a cheap sealing-wax substitute.³ Allgemeine Elektrizitäts-Gesellschaft obtain a soluble condensation product from formaldehyde and aniline in the presence of a polybasic acid, particularly phthalic acid.⁴ I.G. Farbenindustrie⁵ claim to produce a resin of superior solvent properties by condensing formaldehyde in dilute alcohol solution in the *absence* of acid or alkali. The resulting mixture of oil and water is subjected to vacuum distillation to yield a hard resin soluble in a good range of solvents and suitable as a protective coating. No infusible product similar to bakelite is mentioned.⁶

A bone or horn substitute is produced by condensing aniline or toluidine in an acid medium with formaldehyde below 100° . The red product on treatment with alkali gives a horn-like mass.⁷ A preliminary condensation between the amine and formaldehyde may be first carried out in alkaline solution and the intermediate product condensed with more formaldehyde in acid solution. Organic bases

(pyridine or methylamine) or organic acids are used as condensing agents. Similar horn-like products are obtained by condensation in acid solution with addition of ammonium or calcium chlorides.

Benzyl-aniline-formaldehyde condensations have been studied by Herzog.⁸ Nine parts of benzyl-aniline are condensed with 10 parts of 40 per cent. formaldehyde in the presence of hydrochloric acid by heating under a reflux condenser. The top layer, smelling strongly of benzaldehyde, is poured off and the resinous layer at the bottom is washed with water and dried at 110°. A hard, brittle, transparent yellow resin is obtained. It is soluble in benzene and trichlorethylene and in hot turpentine.

According to a patent by the Höchst Farbwerke⁹ solutions suitable for quick-drying varnishes can be obtained by condensing a monocyclic aromatic amine in admixture with α - or β -naphthylamines with formaldehyde; resinous products comparable with colophony were obtained from the naphthylamines alone, but they were less stable to light than the former.

The Society of Chemical Industry in Basle¹⁰ produce a bubble-free resin by condensation of a primary aromatic amine with formaldehyde in an acid medium, and treating the product with a further quantity of formaldehyde. Another patented process is to work up an aromatic amine with an aldehyde in the presence of accelerators and fillers, using heated rollers to give the desired consistency, no solvent being used. The same firm has introduced a process in which the fusible product of condensation in an acid medium is further combined with an aldehyde, e.g. furfural aldehyde, at 140°, a filler being added if desired, and the product hardened by heat and pressure. The use of the filler assists greatly in the washing and neutralization of the product. Other patents have been taken out by the Society,¹¹ including a process for polynuclear aromatic amino-compounds which have been chiefly concerned with 'non-tracking' boards for electrical purposes;¹² for a protective material during the acid pickling of metals¹³ and for modifications of aromatic amine resins by incorporation of phenols or other condensation products to give heat-hardening resins.¹⁴

Methyl-aniline and methyl-diphenyl-amine may be condensed with formaldehyde in an acid medium to give products claimed to be useful as copal substitutes and in the manufacture of sealing-wax.

Although a condensation of acetaldehyde and aniline occurs to give resinoid Schiff's bases the process is not likely to be developed. Rauch¹⁴ condenses aniline with benzaldehyde, whereby anhydro-benzaldehyde-aniline is formed exothermally. The reaction product is heated to 150° with 25 per cent. HCl until a test portion solidifies on cooling to a hard resin, which dissolves in alcohol with difficulty, but is soluble in benzene and in linseed oil. Reference may be made to articles in *British Plastics*¹⁵ for further details of the amino-formaldehyde resins.

Among recent patent specifications for amino-aldehyde resins may be mentioned:

Allgemeine Elektrizitäts-Gesellschaft¹⁶ treat an arylamine with an aldehyde in an acid medium and dissolve the resin in benzene with the addition of alcohol. The product may be used as an impregnating agent. According to conditions of condensation amine resins prepared in the presence of phthalic acid can be made heat-hardening.

Victor Chemical Works¹⁷ have produced a resinous compound which is the reaction product of formaldehyde and phosphorus amides, e.g. $\text{PH}(\text{NH}_2)_3, \text{PS}(\text{NH}_2)_3$.

Ciba Products Corporation¹⁸ condense aniline and formaldehyde with hydrochloric acid until a gel is formed, which is treated with caustic soda solution before drying. Solutions in chlorohydrins may be used as lacquers.

International General Electric Co. Inc.,¹⁹ condense amines and aldehydes in the presence of an anhydride of a polybasic acid.

The Society of Chemical Industry in Basle treat anhydro-formaldehyde-aniline with aniline and aniline hydrochloride and tung oil to give thermo-hardening products.²⁰

An interesting publication dealing with the reaction between amines and formaldehyde in the presence of formic acid has an important bearing on all amine resins, in view of the formic acid content of commercial formalin. It was found that the aldehyde acted as a methylating agent, although the reaction failed with urea and gave only a resinous syrup with aniline.²¹

H. D. Elkington, from the condensation products of aldehydes and aromatic amines in acid media, obtains transparent resins after neutralization and washing followed by boiling-water treatment for 10 minutes.²²

I.G. Farbenindustrie A.-G. obtain resins from aldol and secondary amines, e.g. $\text{NH}(\text{CH}_3)_2, \text{NH}(\text{C}_6\text{H}_4\text{OH})_2$, soluble in alcohol, compatible with nitrocellulose with good electric properties, and can be used in the preparation of hard and durable polishes.²³

Pyrimidines $\left(\begin{array}{c} \text{CH}=\text{CH} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{---} \quad \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \right)$, e.g. diamino pyrimidine, give resins when condensed with low mol. wt. aldehydes; 2:4:6-triamino-

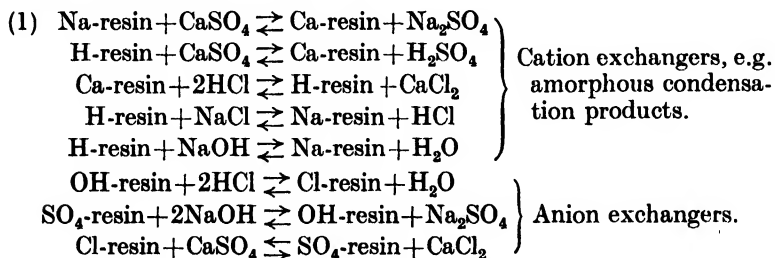
pyrimidine $\begin{array}{c} \text{N}-\text{C}(\text{NH}_2)=\text{N} \\ \parallel \quad | \\ \text{NH}_2\text{C}\cdot\text{CH}\text{---}\text{C}(\text{NH}_2) \end{array}$ is transformed on treatment with hydrazine to 2:4:6-trihydrazino pyrimidine which with CH_2O (30 per cent.) at 60–70° gives a very hard waterproof polymer on stoving over 100°.²⁴

SYNTHETIC RESINS AS WATER SOFTENERS

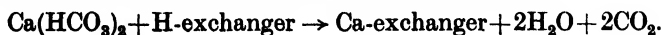
The cation-exchange properties of the synthetic zeolites (sodium silicate-aluminium sulphate reaction product) are well known, whereby the sodium of the silico-aluminium complex replaces the calcium and magnesium of the salts present in the water to be softened; moreover, the activity of the zeolites can be restored by contact with brine and the calcium and magnesium salts removed from the

zeolites. If organic cation-exchange materials be employed, e.g. humic acids (oxycarbonic aromatic compounds which are products of the action of concentrated sulphuric acid on lignite), hot solutions may be used to extract the cations of hard water by hydrogen-exchange. These organic cation-exchange substances go farther than the zeolites in that they may also diminish by cation- and anion-exchange the actual salt content of the water, e.g. the removal of soluble carbonates from boiler water. B. A. Adams and E. L. Holmes²⁵ have drawn attention to the absorptive properties of synthetic resins of the Bakelite class (phenolic), which are *cation*-absorbers, and point out that the amino-formaldehyde resins are *anion*-absorbers for the removal of fluorides, silicates, sulphates, chlorides, &c., from drinking and boiler-feed water. By consecutive use of phenolic- and amino-resins it is possible to effect complete removal of dissolved salts to give a filtrate equivalent to distilled water; this has been proved for tap water, using first quebracho tannin-formaldehyde gel, which removes the cations (Ca and Mg) from hard water, and an *m*-phenylene-diamine-formaldehyde resin to remove anions. It is stated that well water containing 130 parts solid per 100,000 on treatment yielded a final effluent with 0.7 parts solids per 100,000. There is a choice of materials for *anion* absorption in at least three classes, mostly formaldehyde condensation products of (1) aromatic bases, (2) amides, including sulphonamides, (3) proteins.

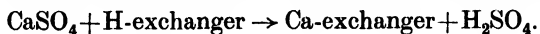
The preparation of various types of ion-exchange resins and their applications in water-softening, the removal of salts from solution by double decomposition, and the purification of organic materials from traces of heavy metals, as well as the separation of basic dyes, are discussed by R. Griessbach and by G. S. Ramshaw.²⁶ Ramshaw illustrates the action of *cation*-exchange resins of the acid or phenolic type and the *anion*-exchange resins of the basic type (amino-formaldehyde resins) as follows:



His conclusions are: (1) In the form of their alkali salts the cation-exchange resins (phenolic type) are suitable for softening water in the same way as do the known base-exchange materials; (2) water rich in carbonates can be partially freed from saline content by passage first through a hydrogen exchange, whereby

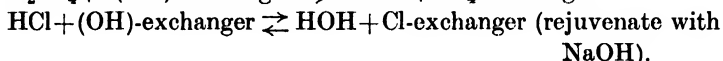
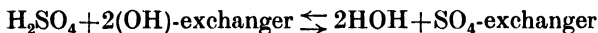
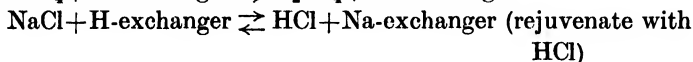
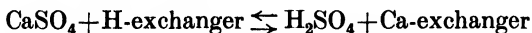


The hardness-forming constituents are fixed by the exchanger also:



The possibility of suitably controlling the range of action of the resin-exchanger is an advantage not common to the ordinary hydrogen-exchangers. By using a buffer filter with the resin-exchanger of average acid strength it is possible to get a water which contains the whole of the carbonic acid in the free form, while the mineral acids remain in the filter in the form of their alkali salts.

(3) Complete removal of all salts from water is made possible by the two-stage process:



(4) It is possible by this means to recover valuable bases (alkaloids, pyridine, &c.) from dilute solutions; also to recover dilute acids (by anion exchange). The separation of basic and acidic dyestuffs and the removal and recovery of traces of heavy metals from water should present no technical difficulties, as well as the removal of iron and objectionable acids from waters and industrial products, e.g. enzyme extracts, sugar solutions, pharmaceutical preparations, &c.

The production of amino-formaldehyde resins has not been commercially successful in comparison with the phenol-formaldehyde resins; nevertheless the anion-absorption property may create a demand for this class of resin.

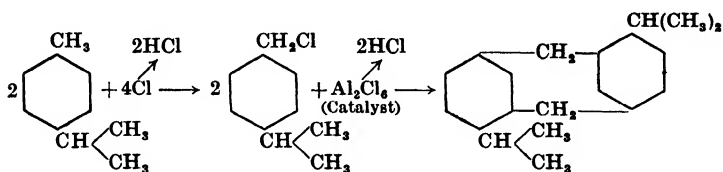
Reference may be made to a recent review of synthetic resins as exchange adsorbents by R. J. Myers and J. W. Eastes (Resinous Products and Chemical Co., Inc., of Philadelphia).²⁷

CHLORINATED HYDROCARBON RESINS

Resins from chlorinated cymene. P. H. Groggins²⁸ chlorinates *p*-cymene in the presence of metals (aluminium, iron, or zinc), producing compounds which condense to form resins. By the addition of other substances, e.g. *o*-dichlorobenzene or naphthalene, the resins can be modified to give more weather-proof and harder coatings. They are insoluble in acids, alkalis, and ethyl alcohol, and are not affected by hot 15 per cent. sodium chloride solution. The resins are produced by low-temperature chlorination, in which ring chlorine substitution is the primary action, and are more stable than those which contain a preponderance of side-chain chlorine atoms. The cymyl chlorides formed as intermediate products have toxic properties and are known to be lethal to small animal and vegetable

organisms. Their vapours are distinctly irritating to the mucous membranes of the eyes, nose, and throat. By incorporating the proper ingredients with *p*-cymene during chlorination it is possible to give specific properties to the final resin. It appears that a market for coating compositions derived from such resins could be used with advantage in marine work, chemical plants, railroad ties, and telephone poles. Stains, varnishes, and lacquers have been prepared from these resins, using *o*-dichlorobenzene and *p*-cymene as thinners.²⁹ They are soluble in turpentine and to a lesser degree in petroleum. When incorporated in lacquers satisfactory *black* pliable coating compositions can be prepared without the use of extraneous pigments. They cannot be brought to an infusible form by heat or pressure treatment. A sample submitted to the Bureau of Standards (U.S.A.) showed a dielectric constant 2.5; power factor 3 per cent.; resistivity 10^4 ohms cm.; dielectric strength 20 kV per mm.

The following scheme may be taken to represent the chemical changes in the formation of a dimer, but in the thermoplastic resin state an open-chain formula is most probable.²⁸



The chemical effect of aluminium chloride as a polymerization catalyst is very complex.²⁹ The resins contain 10–30 per cent. chlorine, therefore some substitution takes place in the cymene ring or the resinous state is reached before all the side-chain chlorine has been liberated. The mechanism of the reaction depends on the presence of metallic chlorides formed by the action of hydrochloric acid liberated by the metal used. The amount of side-chain substitution increases with the temperature of chlorination. When aluminium rods are used at 50° , 30.5 per cent. chlorine is absorbed; whereas, if iron be used at the same temperature 34.85 per cent. chlorine is absorbed, but aluminium gives a more viscous solution of a black resin.

Chlorinated naphthalenes.³⁰ The melting- and boiling-points of chloronaphthalenes increase with the number of chlorine atoms in the molecule, and the melting-point range of the commercial products is 60 – 125° . They are hard, impervious to moisture, and do not burn. Their specific inductive capacity varies with the chlorine content, but on the average it is twice that of paraffin waxes, and their use instead of paraffin and beeswax for condensers and impregnating coils for flame-proofing may be considered.³¹ Seekay (Seekony) Wax (I.C.I., Ltd.) and Halowax (Bakelite Co.), are examples of these substances. Condensers made with chlorinated naphthalenes have breakdown voltages as high as those with paraffin.³² The relation of chlorine content to physical properties of chlorinated paraffin has

been discussed by F. T. Gardner.³³ The chlorination of acenaphthene, fluorene, and indene is also claimed to give varnish resins.

The toxicity of chlorinated naphthalenes increases with the chlorine content, but it is less than that of the chlorinated diphenyls and the effects are confined to liver trouble.³⁴ Chlorinated naphthalene and decahydronaphthalene emulsions with sulphonated mineral oils have been put forward by the I.C.I. as insecticides and fungicides.³⁵ They also claim compositions for use in the manufacture of paints, plastic masses, luting materials, adhesives, moulding compositions and flame-proofing impregnants for cables and films, comprising a condensation product of a partially chlorinated naphthalene (containing < 20 per cent. chlorine) with CH_2O , or a polymer thereof, with which is incorporated a plasticizer of a chlorinated hydrocarbon of high mol. wt., e.g. chlorinated rubber, &c.³⁶

Benzyl chloride resins. If benzyl chloride be mixed with 1½ per cent. anhydrous ferric chloride, reaction proceeds at the ordinary temperature to yield a porous dark-brown solid mass, which is purified by steam and the last traces of iron removed by hydrochloric acid. The resulting resin is of a yellowish colour, soluble in benzene, chloroform, and cyclohexanol, but not in alcohol. The lacquer film resists the action of acids and alkalis. In the place of benzyl chloride, *o*-chlorobenzyl chloride and chloromethyl-naphthalene may be used. Heat is needed if aluminium or zinc chlorides are employed.³⁷

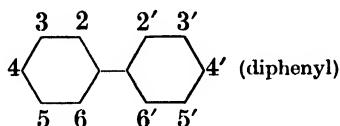
Further extension of the process can be applied to the interaction of a hydrocarbon with a chlorinated hydrocarbon, e.g. benzyl chloride condenses with naphthalene to give oily products, whereas xylyl dichloride with naphthalene gives a solid resin.³⁸

As catalysers, iron or iron compounds and aluminium powder or copper bronze may be employed.³⁹ The substances may be used as impregnating compounds with cellulose.⁴⁰ In one example, from naphthalene and benzyl chloride on heating in air at 170–90° in the presence of manganese dioxide or ferric chloride, a brown resin is obtained, soluble in linseed oil and acetone and aromatic hydrocarbons. The films are said to be weather resisting. Substances, e.g. phenol, naphthalene, cresol, after condensation with benzyl or xylyl chloride can be oxidized in the presence of manganese dioxide or ferric chloride to give brown resins.⁴¹

Treatment with formaldehyde and acetic acid in the presence of zinc chloride in small amounts improves the products considerably,⁴² e.g. from naphthalene and xylyl chloride with formaldehyde a resin is obtained giving lacquers fast to light; these are neutral and soluble in linseed oil. Xylol and ethylene chloride with 3 per cent. AlCl_3 give oily products, which on stronger heating give resinous masses.⁴³ Naugatuck Chem. Company⁴⁴ prepare plastic materials, resistant to abrasion and water, acids and alkalis by condensation of aromatic compounds ($\text{R}-\text{C}_6\text{H}_4-\text{R}_1$) in the presence of AlCl_3 . Emulsifying and frothing agents are produced by condensing benzyl chloride with naphthalene sulphonic acid in the presence of sulphuric acid.⁴⁵

CHLORINATED DIPHENYL RESINS

Chlorinated diphenyl. Chlorination of diphenyl (98.5 per cent. technical) gives 2- and 4-monochlor-isomers:



2-monochlor, m.p. 32°; b.p. 273.4°.

4-monochlor, m.p. 77°; b.p. 291°.

3 parts of [2-] and 1 part of [4-] give a eutectic mixture, m.p. 14°, b.p. 278-95°; s.g. 1.1567 25°/25°; flash-point 127-9°; viscosity (Saybolt) 30 sec. at 99°.

The monochlor-mixture contains 19 per cent. weight of chlorine and is a liquid with the viscosity of water. *Arochlor* (Aroclor) is a mixture of isomers produced by chlorination up to 66 per cent. chlorine content and varies from a light mobile liquid to a syrup or to a solid resinous or crystalline state, but by careful control of the chlorination and subsequent operations a uniform product can be obtained.

*Influence of Chlorine Content on the Properties of Chlorinated Diphenyl*⁴⁶

No.	Percentage of chlorine	Properties of chlorinated diphenyls
1	18.30	Light mobile liquid.
2	23.19	„ oil.
3	42.11	„ „ s.g. 1.375 at 29°.
4	42.86	Heavier oil.
5	52.15	Viscous oil.
6	57.19	Semi-solid—pitch-like.
7	59.73	Semi-solid—s.p. 49.5°.
8	65.26	Non-crystalline solid, s.p. 61.5°; conchoidal fracture.
9	65.40	Semi-crystalline solid.
10	66.21	Crystalline solid.

	<i>Arochlor 1254,</i> viscous oil, 43% Cl	<i>Techn. Diphenyl,</i> light yellow crystals	<i>Arochlor 1219,</i> water-white liquid	<i>Arochlor 1262,</i> yellow tarry resin, 52% Cl	<i>Arochlor 1268,</i> pale yellow cryst. mass	<i>Arochlor 2565,</i> black resin	<i>Arochlor 4465,</i> pale amber resin	<i>Arochlor 1242,</i> water-white liquid
Melting-point	wax at 0°	68.6	14°	brittle at 0°	127-71°	78°	70°	fluid at 0°
Boiling-point	360-81°	255.6	278-95°	374-410°	395-415°	250-360° (10 mm.)	240-90° (9 mm.)	320-60°
Specific gravity	1.52	1.007	1.1567	1.64	1.8	1.72-1.74	1.71-1.72	1.36
Refractive index	1.6407	..	1.6125	1.6501	1.607- 1.629

Arochlor resins undergo no further condensation on hardening or repeated melting. They are now being produced with softening-points of 70–5°. They are insoluble in water and in glycerol, but are soluble in the usual organic solvents and mineral and vegetable oils.⁴⁷

Information is meagre regarding the chemistry of these resins; they are mixtures of chlorinated diphenyl and polyphenyl derivatives.

H. W. Bowron,⁴⁸ in a survey of chlorinated diphenyl resins, states that their use is among the outstanding recent developments of the paint industry. Arochlors are resistant to water, acids, alkalis, and fire, and exert no corrosive influence on metals; moreover, they have no toxic effect on the skin, but their vapours cause irritation, however, their b.p.s are high.

Tung oil varnishes with arochlors 1254 and 4465 are resistant to water and alkalis, light in colour, and the resins seem to bleach the vegetable oils.⁴⁹ They can be used as plasticizers in cellulose varnishes (arochlor: tricresyl phosphate; 1:1), but in fabric dopes they are unsuitable because of the reduction in tautness of the fabric.⁵⁰ Alone, arochlors are not suitable for waterproofing, but when mixed with other substances are satisfactory. Wood and textiles may be flame-proofed, the resin giving strength to the wood. W. Koch⁵¹ uses them as plasticizers for chlorinated rubber where the important requisites are water-resistance, adhesion, and corrosion-resistance.⁵² Alone they are not promising as moulding compounds, because they are permanently thermoplastic. As electric insulators they are very promising. High dielectric strength and resistivity makes them useful in transformers and as dielectrics for condensers of increased capacity. The British Thomson-Houston Co., Ltd.,⁵³ use 50–5 per cent. chlorine content in condensers because of the low power factor.⁵⁴ Further information as to the dielectric properties of chlorinated diphenyls is given by A. H. White and S. O. Morgan.⁵⁵

As a lacquer component chlorinated diphenyl is employed for its plasticizing properties, and on account of its extremely slight volatility it preserves flexibility in the film.⁵⁶ It may also be used in priming coats and lacquers, because of its powerful adhesion to the smoothest surfaces, especially to metals. Moisture-proof wax coatings containing 10 per cent. wax with arochlors are claimed by Jenkins.⁵⁷

Arochlors 1254 and 1262 are compatible with nitrocellulose and acetate lacquers and form suitable plasticizers; the load/elastic curves show that they confer good mechanical properties on the films.⁵⁸ They may be used as plasticizers for benzyl cellulose.⁵⁹ H. A. Gardner⁶⁰ incorporates chlorinated diphenyl with other artificial resins to form bases for varnishes and lacquers and linoleum compositions; drying-oils, turpentine, &c., may be added.⁶¹ Semi-liquid or hard resins are dependent on the degree of chlorination. Among recent researches and patent specifications dealing with diphenyl resins may be mentioned the following: R. L. Jenkins, R. McCullough, and C. F. Booth⁶² point out that the technical product containing 68–97 per cent. diphenyl cost, in 1930, 40–60 cents per lb.,

or approximately 1 per cent. of its former price. The product of the monochlorination of diphenyl in the presence of $SbCl_5$ or Fe, under low-temperature conditions and less chlorine than the theoretical amount, after removal of the excess of diphenyl by fractional distillation gives a yield of 36.8 and 29.9 per cent. respectively of 2 and 4 chlorodiphenyl and only 2 per cent. dichlorodiphenyl is produced. The degree of chlorination up to octochlorodiphenyl has been examined by F. L. W. van Roosmalin:⁶³ starting from diacetylbenzidine, chlorination was carried to tetrachlorobenzidine and then to tetrachlorodiphenyl and finally to the octo-substance. The Federal Phosphorus Company and Swann Research Inc.⁶⁴ describe a preparation of chlorinated diphenyl at 65°, by chlorination until the density reaches a value corresponding to more than 40 per cent. chlorine, in the presence of iron filings as catalysts, and the product obtained is distilled, b.p. range, 295–345°, 350–80°, and 374–410°. The colour is water-white to yellow according to the degree of chlorination. The physical properties may be varied according to the mode of treatment. I.G. Farbenindustrie, A.-G.⁶⁵ use antimony pentachloride as catalyst and chlorinate at 70°, keeping the mass just fluid. When about 160–200 parts of chlorine have been introduced for 500 parts of diphenyl the temperature is about 10°. After the introduction of 1,500–2,000 parts of chlorine, the hydrochloric acid is driven off by a current of air. The resin (Clophen) is purified by an alkaline agent and distilled, b.p. 225–45° (12 mm.), and contains 63 per cent. chlorine. Corresponding to hexachlorodiphenyl is a hard solid, m.p. 30°. Jenkins and J. A. Sikarski⁶⁶ (Swann Research Inc.) claim for the production of transparent chlorinated diaryl resins; e.g. a transparent non-crystalline solid at ordinary temperature and suitable for use as a varnish resin is obtained by chlorinating diphenyl together with other diaryls in the presence of iodine. With iron as a catalyst the dark chlorinated product containing up to 66 per cent. chlorine may be distilled to give colourless or light yellow resins. With larger chlorine-content crystalline substances are produced. *Permitol* is tetrachlorodiphenyl.

The production of mono- and dichlor-isomers of diphenyl, by dissolving diphenyl in a liquid mixture of higher chlorinated diphenyls and chlorinating whilst in solution, is claimed by the Swann Research Inc.⁶⁷ (now the Monsanto Chemical Co., U.S.A.), and these compounds are generally for use in the electrical industry.⁶⁷ The possible structure of these resins will be discussed in the chapter on Problems of Resinification.

CHLORINATED METASTYRENE RESINS

When chlorine is passed into a solution of metastyrene in carbon tetrachloride in the dark and at 0° in the presence of iron filings, a chlorinated product is obtained, less thermoplastic than metastyrene, and if made from a high polymeride may be used in spraying.⁶⁸

The chlorinated rubber resins have been described on pages 326–8.

FURFURALDEHYDE RESINS

Furfural (furfuraldehyde), $C_4H_3O \cdot CHO$, is an extremely reactive substance, and both its physical properties as a solvent and its chemical reactivity suggest many possibilities of industrial application. Its chief physical characteristics are: b.p. 161° ; s.g. 1.1598^{30} (pure), $1.159-1.160$ (technical); freezing-point -36.5° ; refractive index, n_D^{20} , 1.52608 , flash-point $55-7^\circ F$. Furfural resinifies in the presence of hot alkali to a black insoluble resin. Condensation resins can also be made from furfural and phenol, but the reaction is not so satisfactorily carried out as with formaldehyde and phenol. These resins may become of increasing interest to the varnish manufacturer owing to the cheapening of the production of furfural from corn-cobs and oat-hulls. Furfural was first made in any appreciable quantity by Stenhouse⁶⁹ in 1840, who treated oatmeal and sawdust with sulphuric acid. The process has been developed by the Miner Laboratories of Chicago, who can produce furfural in large quantities from oat-hulls, a by-product of Quaker Oats. A yield of about 10 per cent. on the weight for the raw material is obtained. The industrial uses of furfural are so far not extensive, but the largest commercial application of furfural as yet developed is in the manufacture of moulding resins and compositions.⁷⁰

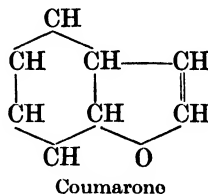
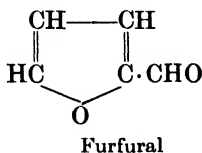
The oat-hulls, obtained in the process of making rolled oats, are a convenient source of furfural, and as the result of careful study it has been possible to reduce the price to about 15 cents a lb. in 30-ton lots, whereas 10 years ago the price was about as many dollars a lb. and only very small quantities were available. Although comparatively simple, the development of an economic process presents technical difficulties. All that is necessary is to hydrolyse the pentosans with mineral acid and separate the furfural by steam distillation. The distillate consists of two layers, the upper containing 84 per cent. of the furfural and the lower 18 per cent. By choosing the optimum conditions the steam consumption (calculated on the raw materials) has been reduced to one-quarter, whilst a specially designed apparatus has rendered it possible to recover much of the furfural in the aqueous layer and to produce an article of 98-99 per cent. purity.⁷¹ Another interesting process of furfural preparation utilizes cellulose raw material.

Sawdust or wood shavings are hydrolysed by concentrated hydrochloric acid and the product is treated under pressure at 100° with gaseous sulphur dioxide and steam, when the sugars are transformed into furfural. The yield is equivalent to 25 litres of furfural from 100 kilos of cellulose material.⁷² Among European sources of supply, a prominent place is taken by the waste seed-husks of the sunflower, which is cultivated on an enormous scale, notably in Russia.⁷³

The spent acid sulphite liquors from the digestion of wood for furfural manufacture are the subject of a patent by A. Richter.⁷⁴ Blomquist and Groth⁷⁵ have proposed a process for working up pentosan-containing raw material to furfural by hydrolysis.

Corn-stalks are another waste material the treatment of which for furfural production presents possibilities. Darling's method is to treat the stalks with very dilute caustic soda of such strength (1 per cent.), that, when substantially the whole of the lignin has been dissolved out, the residual free alkali is too small in quantity to react with the xylan, which is then converted to furfural.⁷⁶

The structural formulae of furfural and coumarone:



indicate that resinification may proceed along the same lines as that of coumarone, and at the same time the presence of an aldehyde group indicates the possibility of condensation with phenols, amines, and similar substances to give resins.

As regards commercial development, the use of metals (Fe, Ni, and Pb) or metallic chlorides (AlCl_3 and FeCl_3) as catalysts appears to be the more important, and the resins obtained by direct polymerization of furfural have thermo-hardening properties and resemble the phenol formaldehydes and glyptals rather than the coumarone resins. With aluminium chloride at 100° a gelatinous substance is obtained soluble in acetone, which is fusible, and can be converted to an infusible and insoluble form on further heating.⁷⁷ It would appear that polymerization as distinct from molecular condensation occurs due to the presence of the aldehyde group. The resins obtained with alkaline catalysts are dark in colour and soluble in alcohol, benzene, and furfural. They can be used as stains and, owing to the high penetrating power and fungicidal properties of furfural, their use for decorative and preservative purposes on wood presents considerable possibilities. A varnish resin has been made from furfural and aniline with ammonia, caustic soda, or potash by heating for 3 hours in a closed vessel at $140\text{--}50^\circ$, or 40 hours at $70\text{--}80^\circ$.^{78,79} Acetone gives similarly a resin with furfural. A number of aromatic amines give resins with furfural,⁸⁰ which are soluble in alcohol, benzene, and furfural itself. A general survey up to 1923 is given by Trickey, Miner, and Brownlee of the Miner Laboratories, and up to 1935 by Fr. Peters of the Quaker Oats Company, who lays stress on the value of furfural as a solvent for potentially reactive phenolic resins as well as for many naturally occurring gums. This discovery resulted in its widespread adoption as a solvent in the manufacture of resin-bonded abrasive wheels. For years furfural has enjoyed pre-eminence in this field, and no solvent has yet been equally suitable. The importance of this type of grinding wheel can be appreciated (according to Peters) from the fact that the grinding costs incident to the

manufacture of moderate-priced automobiles have been reduced by 80 per cent. during the last ten years, and wheels in which furfural was used have been largely responsible for this economy.⁸¹

Black furfural acetaldehyde resins are produced by condensing furfural with acetaldehyde in the presence of a mineral acid (conc. HCl). The ebonite-like moulding products possess considerable mechanical strength and chemical resistance and are lighter or heavier than water according to conditions of preparation.⁸² Furfural condenses with ammonia under pressure at 120–40° forming a resin suitable for dark-coloured moulding powders and varnishes.⁸³

FURFURYL RESINS

Furfuryl alcohol ($C_4H_3O(CH_2OH)$) on polymerization by a catalyst yields a resin; G. Roberti and D. Dinelli use 1 per cent. iodine in an autoclave at 100°.⁸⁴ A yield of 90 per cent. of a hard resin ($C_9H_5O_2$) with satisfactory elastic, mechanical, and electric properties is obtained. G. Roberti also obtains elastic rubber-like substances by heating furfural, furfuryl alcohol, or tetrahydro-furfuryl alcohol in the presence of an acid, e.g. HCl. Glidden Co. obtain a composition consisting of partly polymerized furfuryl alcohol in a solvent which retards further polymerization, but just before use a polymerization promoter is added, and the resulting film is highly acid and solvent-resisting.⁸⁵

PHENOL-FURFURAL RESINS

Beckmann and Dehn⁸⁶ studied the reactions of furfural with 24 phenols, using acids, acid salts, and alkalis as condensing agents. They found that the proportions of phenol and furfural required for resinification to the infusible condition were equimolecular, whereas excess of phenol gave jelly-like masses. The range for a fusible product with furfural and phenol using hydrochloric acid is 10–20 per cent. furfural based on the phenol. Alkaline catalysts, e.g. sodium carbonate, give rise to insoluble resins with the proportions of 1.25 mols. of furfural to 1 mol. of phenol. The condensation is so rapid that it may become almost uncontrollable, and in order to moderate it a large excess of phenol must be used; the velocity of reaction is also influenced by temperature and by the concentration of the acid.

Beckmann and Dehn obtained a soluble fusible resin from a ratio of 10 of phenol to 1 of furfural, whereas with the proportions of 5–1 the resin is a rubber-like insoluble mass. The Quaker Oats Co. patented black-coloured products using hydrochloric acid as condensing agent.⁸⁷ Mains⁸⁸ obtained reddish-brown resins by condensing tar oils containing xylene with furfural, using sodium carbonate as catalyst. The resin is solid in furfural, acetone, and alcohol-benzene. It can be hardened by admixture with paraformaldehyde, furfuramide, or hexamethylene-tetramine. The furfural may be replaced in part by formaldehyde, whilst methyl-furfural can be

used as a substitute for furfural itself. Both lacquers and moulding powders can be produced which incorporate resins of this type.

Durite belongs to the class of phenol-furfural and phenol-formaldehyde resins, in the form of permanently fusible or potentially reactive resins, as crushed, pulverized, liquid, or varnish forms; as thermo-setting varnishes for impregnating, laminating, and coating materials in the manufacture of hot-pressed sheet-stock, gears, decorative panels; as resins for bonding hot or cold mouldings, compositions, high-speed grinding, and cut-off wheels, abrasive articles, &c.; as oil-reactive and oil-soluble resins for the manufacture of quick air-drying and baking varnishes; as heat-setting cements for basing incandescent lamps and radio valves and for technical purposes; as compounds for hot-press mouldings of lasting durability. The unique characteristics and the natural brown or black colour of the phenol-furfural resin binder assure mouldings of exceptional beauty, smoothness of finish, and dimensional exactness with improved colour, permanency against light acids and weak alkalis (*Durite* Plastics, Division of Stokes and Smith Company).

The resins obtained by the above processes are dark in colour. O. Routala and O. Kuula⁸⁹ state that molecular amounts of furfural and phenol with alkalis or lime as catalysts yield soluble black resinous products; furfuramide can be used in place of furfural. The resins can be bleached by halogens. Furfural and acetone give a whitish resin whose quality is improved by rosin. The soluble resins are heat-convertible. With acid catalysts hard, insoluble, black resins are immediately produced in the condensation of molecular amounts of furfural and phenol. A variation consists in condensing the furfural with a phenol-aldehyde condensation product.⁹⁰ The resin when mixed with an acid catalyst slowly hardens, but remains in the plastic condition long enough to be worked with a knife.

Tzonev and Yavnel⁹¹ have examined the resinous condensation products of furfural with a variety of phenols. Of the cresols, the *meta*-isomer reacts with the greatest rapidity, whilst the *para*-compound is the slowest. A similar order of reaction velocity was observed in the case of the three isomeric dihydroxy-phenols. β -Naphthol is the most active of the naphthols in condensation with furfural. They generalize that the hardest resins are formed from the least symmetrical molecules; *meta*-cresol-furfural resins are harder than the corresponding phenol resins, whilst the resorcinol resins are the hardest.⁹² The same investigators produce resins from sunflower seed-husks with phenol at 100°, in the presence of a mineral acid. The plastic masses are not equal in quality to those resulting from the condensation of phenol with purified furfural. Good moulding qualities are claimed by O. A. Cherry and F. Kurath⁹³ by condensing phenol with about $\frac{1}{3}$ of its weight of furfural in the presence of 16 per cent. caustic soda solution.

An impregnating material for paper and other fibrous materials is formed by the reaction of a furfural solution of tung oil with the previously prepared phenol-furfural product. Freedom from tackiness

at the ordinary temperature is claimed for impregnated products which are suitable for moulding.⁹⁴

Phenol-furfural resins are compatible with cellulose acetate, and their use in the manufacture of dope and insulating varnishes may be worthy of further investigation. Furfural is a solvent for cellulose acetate, and Ellis describes a process in which cellulose acetate or nitrate is dissolved in furfural and then, by the action of an acid catalyst, the furfural is resinified. The presence of the cellulose acetate is stated to improve the plastic properties of the product.⁹⁵

The Bakelite Corporation finds it advantageous in the preparation of phenol-furfural moulding compositions to produce a reactive resin (comparable with Bakelite 'A'), which is incorporated with an accelerator consisting of an alkaline earth oxide and hexamethylenetetramine, e.g. furfural, cresol, or phenol, are refluxed with a little sodium carbonate and, after expulsion of water and addition of the alkaline earth oxide (lime) and the 'hexamine', the mixture is heated to 100-40°, until a thick fusible mass is produced. After incorporating fillers a rapidly curing moulding composition is obtained.⁹⁶

Furfural resins as electrical insulating material have been discussed by W. Ogaur, T. Hanya, and T. Yanagihashi.⁹⁷

E. E. Novotny has reviewed the manufacture and uses of phenol-furfural resins.⁹⁴ F. N. Peters of the Quaker Oats Co., Chicago, states that the phenol-furfural resins are strong, elastic, and heat, acid, and alkali resisting resins, with good mechanical strength and electric properties. He points out that furfural and its derivatives (furfuryl alcohol and tetrahydro-furfuryl alcohol) are solvents for cellulose esters, phenolic resins, certain natural gums, &c.⁹⁹

ACETONE-FURFURAL RESINS

Ketones will condense with furfural to a resin useful in the formation of cellulose acetate lacquers, which may be produced by heating 100 parts furfural with 100 parts acetone and 4 parts 50 per cent. caustic soda solution under reflux for 1 hour. A comparatively light-coloured resin is produced melting at 90-100°. ¹⁰⁰ The durability of varnishes containing acetone-furfural and acetone-furfuramide resins is noteworthy. O. Routala and O. Kuula¹⁰¹ claim that replacement of part of the acetone by rosin is an improvement. Acetone-furfuramide varnishes are very durable, especially by addition of rosin. Furfural and its derivatives produce resins with methyl-ethyl ketone as well as acetone with caustic alkalis.¹⁰²

OTHER FURFURAL RESINS

Urea-furfural resins. A method for the production of thermosetting resins is described by Novotny and Johnson,¹⁰³ whereby urea and furfural are heated at 105° with ammonia for 2 hours; water is distilled off, leaving the residual resins. The subsequent rate of hardening is increased by the presence of agents containing methylene groups.

Aniline-furfural resins. Deep black resins are produced on

condensing furfural with aromatic amines. They are useful in the application of cellulose acetate lacquers, owing to the characteristic incompatibility of this ester with most natural and synthetic resins, leading to clouding in the solution or the film, this defect is avoided by the presence of the compatible aniline-furfural resin.¹⁰⁴ The use of rosin, which has been already referred to, is the subject of patents by Cherry and Kurath,¹⁰⁵ in which rosin and aniline are first heated together, with subsequent addition of furfural and further heating; the product is said to be less brittle than rosin and to exert a plasticizing action upon phenolic moulding compositions. Naphthylamine, toluidine, and xylylene may replace aniline.¹⁰⁶ An amino-furfural resin bleaches on exposure to light, whilst a phenol-aldehyde resin darkens.

Furfural-amino-fatty-acid condensations. Stearic acid and aniline giving an anilide condense with furfural at 200° to give a dark brown wax, which is a useful ingredient of phenolic moulding compositions, acting as a lubricant, a plasticizer to improve flowing properties during moulding, and finally as a darkener of the colour of the mouldings. Oleic acid gives a black viscous oil, whilst benzoic acid with stearic acid furnishes a black waxy substance.¹⁰⁷

Plastic, elastic, and flexible substances may be obtained by interaction of furfural with alkaline polysulphides.¹⁰⁸

Vinyl-furfural-aldehyde resins. The General Electric Co. obtain a hard, tough, moisture-resistant compound comprising the product of heating a solution containing furfural and the products of the reaction of an aldehyde, e.g. CH_2O , with hydrolysed polymerized vinyl acetate or the like at a temperature high enough to volatilize the uncombined furfural. 2-vinyl-furan plastic products are polymerized in aqueous emulsion to latex-like polymerized to give thermoplastic materials forming films of good quality.^{108A}

LIGNIN RESINS AND PLASTICS

Lignin resins. Lignin (obtained from waste sulphite liquor) may be dissolved in phenols and the mixture heated with an aldehyde.¹⁰⁹ Specially treated cellulose material and waste sulphite liquor may be used.¹¹⁰ Sawdust may be subjected to acid hydrolysis and pressed with aniline or formaldehyde to yield moulded articles;¹¹¹ the optimum content of lignin in the sawdust varies according to its origin, being 43-5 per cent. for pine, 35 per cent. for spruce, and 89 per cent. for birch.¹¹² Potato starch is also claimed as a raw material for plastic manufacture; it is heated with CH_2O and caused to react with phenol and urea.¹¹³ Lignin furfural resins are being investigated as a source of pre-fabricated building materials which, as the cost of furfural decreases, will become attractive.

Lignin plastics. In Canada and in the U.S.A., as well as in Japan, considerable research has been directed in recent years to finding a commercial outlet for lignin and its derivatives. It is estimated that the pulping liquors from the paper industry can supply one and a half million tons of lignin annually, and several

additional million tons could be obtained from forest or saw-mill wastes. Lignin is an important constituent of the cell-wall consisting of a cellulose base compounded with aryl derivatives, but its precise chemical structure is not yet known. Some success has been achieved by means of hydrogenation, especially in conjunction with the butyl alcohol pulping of wood, whereby lignin is removed in a comparatively unchanged condition free from organic salts. The hydrogenation of the lignin in dioxane solution at 250° and 200–300 atm. pressure with a copper-chromium oxide catalyst yields 26 per cent. methyl alcohol, 38 per cent. propyl-cyclohexane, and as much as 60 per cent. of a high-boiling resin. The lignin in this case is obtained from hardwood by the action of methyl alcohol and hydrochloric acid, and identified products amount to 80 per cent. of the original material (E. F. Harris and collaborators).¹¹⁴ In connexion with the high yield of the resin the Menasha Co. has recently installed a large plant to make plastic material from sulphite pulp lignin at about one-third the cost of similar plastics. Lignin obtained in other ways than with acidified alcohol, e.g. that isolated from soda-pulping liquor or with sulphuric acid from other soft or hard woods, can be readily hydrogenated.

Little success had been achieved in the utilization of sulphite liquors until the hydrogenation process showed a more promising way. The greatest promise is in the direction of a cheap and commercially feasible method of hydrogenation, which would open the way to the preparation of many valuable organic compounds. Among other methods already developed are: (1) Forest Products Lab.¹¹⁵ treat hydrolysed sawdust with a plasticizer and mould under pressure and heat to give dark-coloured lustrous articles; (2) G. C. Hayward¹¹⁶ treats the product resulting from the action of alkali and heat on the calcium salt of lignin sulphonic acid to be compounded with wood fibre to furnish laminated sheets and strong hard boards; (3) Mead Corporation¹¹⁷ precipitate with carbon dioxide the soda liquors of pulped hardwood to produce a lignin with enhanced chemical activity. Among the many uses of these lignin products may be mentioned tannin substitutes, water-softeners, additions to cement to increase water-holding properties, and depolarizers to negative plates of storage batteries with great increase in output at temperatures below zero.¹¹⁸

Summary. In his review of the properties of this class of resins Peters points out their superiority as sealing material of electric-light bulbs to their brass bases. Moreover, furfural and furfuryl alcohol resinify to form insoluble products (cf. Roberti, below), and this reaction affords an excellent method of impregnating porous materials with the subsequent formation of a resin *in situ*. There is even a patent suggesting the use of furfural with sea-weed to give resins;¹¹⁹ another patent describes the use of the resin obtained by evaporation of furfural as a coating composition for copper wire; resins of furfuryl derivatives with methyl acrylate are also mentioned. Peters (loc. cit.) considers that the furfural resins have a

great future. The restrictions as to development are due to the present price of the raw material and to lack of research on their properties. He considers that in twenty-five years furan chemistry will be established industrially as is the chemistry of aromatics.

RESINS CONTAINING SULPHUR

The introduction of sulphur into formaldehyde-cresylic resins appears to augment their insulating properties, and activity is to be noted in France in connexion with such resins.¹²⁰

Thiolite is prepared by condensing formaldehyde and cresol up to such a point that the product is still soluble in alcohol and acetone. The product is treated with sulphur chloride, hydrochloric acid is eliminated, and a product is obtained with a content of sulphur amounting to 12 per cent. It is purified by successive solutions and precipitations, with alcohol as solvent and water as precipitant. *Thiolite* softens at 80° and subsequently melts. If pressure be introduced at this point hardening takes place. It may be moulded at 150° in a hot press. Before hardening it is soluble in alcohol, hydrocarbons, acetone, and pyridine. The insulating resistance of this resin is 300×10^6 megohm-cm.³, and its dielectric constant is 4.5.¹²¹

Karbolite is a Russian product obtained by condensing phenol and formaldehyde in the presence of a sulphonated mineral oil, i.e. naphtha-sulphonic acids.¹²² K. Tarassoff condenses formaldehyde with the products made by heating phenol with turpentine together with naphtha sulpho-acids to obtain elastic soluble resins.¹²³ Non-colouring thio-derivatives of phenol are made from soluble formaldehyde, paraldehyde, or acetaldehyde resins by the action of alkalis and sulphur or alkali or alkaline earth polysulphide. It is to be noted that β -naphthol and acetaldehyde do not resinify, but give colourless needles, m.p. 170–80°.¹²⁴

Resinous products suitable for leather varnishes may be produced by heating excess of aromatic hydrocarbons with an arylsulphonic acid or sulphuric acid in the presence of sulphur. Increased proportion of sulphur reduces the solubility of the resin.¹²⁵

Ethylene polysulphide products are stated by W. H. Stevens to be used in making oil-resistant printers' rollers.¹²⁶

Ethanite is a resin made from ethylene dichloride and potassium polysulphide by Wilfred Smith, Ltd., London.

Resins may be obtained from primary and secondary aryl-amines, except *p*-toluidine and *N*-alkyl-anilines, when these are heated with sulphur with or without iodine as catalyst; 1 mol. of aniline and 2 mols. of sulphur at 185–220° give a pale-yellow resin containing 36.5 per cent. sulphur, soluble in acetone, m.p. above 15°; with 44 per cent. sulphur, the resin softens at 100° and becomes infusible on further heating.¹²⁷

Thiokol (Thiokol Corporation) is made by interaction of $\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{Cl}$ with Na_2S_4 and forms a polymer having the empirical composition $(\text{CH}_2 \cdot \text{CH}_2\text{S}_4)_n$. It is an elastic rubber-like substance

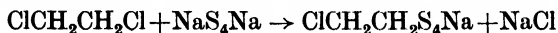
resistant against oils and hydrocarbon solvents when heated above its melting-point, 70°.

Thiokol is stated to be used extensively for the lining of hose carrying petroleum fuel and paint and lacquer solvents. In the printing industry it is used for rollers and offset blankets, because of its resistance to printing-ink ingredients.

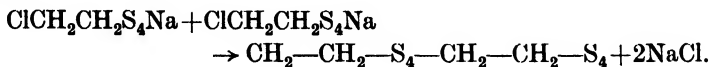
Thiokol is also used in sheathing for cable, where it replaces lead to some extent, being more flexible and not subject to electrolysis, especially in underground cables.¹²⁸ By compounding with natural rubber there is a marked increase in the ageing properties of the latter. It may be used for gaskets by impregnating carton paper with thiokol cement, also for washers for insulating the ends of ignition condenser cases because of the good oil-resistance. A disadvantage of this type of plastic is the odour, although recently there has been improvement.

Cotton fabric coated with 3 oz. thiokol per sq. yd. will allow hydrogen gas to permeate at the rate of 0.01 cub. ft. per sq. yd. in 24 hours, whereas a similar coating of rubber has a 70-times greater permeability.¹²⁹ Fabrics coated with polysulphides show distinct advantage over fabrics coated with hydrophylic colloids, e.g. gold-beater's skin and gelatin. The relatively large size of the sulphur atoms in thiokol may account for the impermeability due to high structural density. G. F. Esselen and F. S. Bacon point out the relative cheapness of production of thiokol and anticipate increased demands for its use.¹³⁰

Processes for the production of polysulphide plastics include condensation of ethylene halides with alkaline sulphides or condensation of the latter with aldehydes or ethylene dichloride, and glycerol dichlorohydrin with sodium polysulphides. The mechanism of the reaction has been fully discussed by J. C. Patrick who represents the reaction of ethylene dichloride and sodium tetrasulphide as:

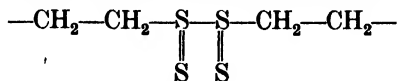


and



The polymer has properties as regards extensibility and retractability comparable with natural rubber (Wingfoot Corporation, U.S.P. 2,067,465; B., 1938, 1192). This rubber-like property is stated to be connected with co-ordinate linkage of two of the sulphur atoms of the S₄ complex.

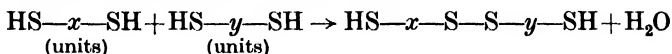
A tentative formula for the rubbery tetrasulphide polymer is:



Two of the sulphur atoms appear to be bound differently and may be removed without degradation of the linear molecule, but with

the loss of rubber-like properties. The analogy of the physical properties of rubber with those of the polysulphide polymers is worthy of careful consideration (cf. Chapter XII, p. 324).¹³⁰

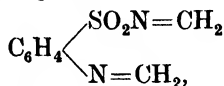
If the plastic material of the thiokol be mixed with zinc oxide or an oxidizing agent, e.g. benzoyl peroxide, and heated to 140°, when stretched and released it retracts with a snap and becomes very elastic, comparable with the vulcanization of natural rubber. It is considered by Patrick (loc. cit.) that the product of the curing process contains mercaptan terminals (SH):



while water is split off, the zinc oxide acting as an oxidizing agent.

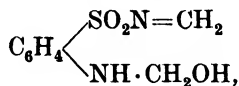
SULPHONAMIDE (SULPHAMIDE) RESINS

Condensation of formaldehyde with aryl-monosulphonamides gives resins of a fusible and soluble type, whereas di- and trisulphonamides give hard and insoluble resins. Aniline *o*-sulphonamide with formaldehyde gives:



a fusible resin, m.p. 100–18° and final m.p. 105–57°. It is not monomolecular.

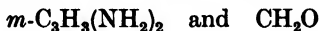
Aniline *p*-sulphonamide or *m*-sulphonamide with formaldehyde gives



a methylenemethylol compound, which contains more than one reactionable group, and it is an infusible resin. Not only the number but the position of the groups is necessary to give resins which harden on heating. The hardening property seems to be connected with the possibility of a polydimensional representation (at least a 2-dimensional ring system); 1-dimensional resins do not attain marked hardening, so that the consideration of the ring formation is essential. G. Walter¹³¹ claims for furfural and aromatic sulphonamides, containing in addition to one SO_2NH_2 group at least one substituted or unsubstituted NH_2 group; the product may be used for lacquers and moulded articles.

p-Toluene sulphonamide is a by-product in the manufacture of saccharin and condenses with formaldehyde to yield resins soluble in alcohol and acetone, compatible with cellulose esters and ethers and unaffected by light; they are soft, and W. H. Moss and A. H. White recommend additional *p*-toluene sulphonamide and further heating.¹³² Xylene disulphonamides and benzene *m*-disulphonamides, disulphonamides of phenol, and sulphonamides of carboxylic acids have been condensed with formaldehyde. The sulphonamide resins

containing HSO_3 groups have base (cation) exchange properties, e.g. the resin may be prepared by condensation of $p\text{-(OH)C}_6\text{H}_4\text{SO}_3\text{H}$ with CH_2O or by sulphonating a previously prepared resin, e.g.

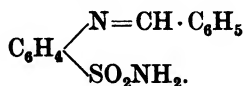


(cf. p. 334).¹³²

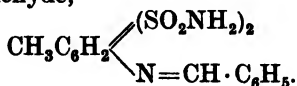
The composition and properties of some of the aryl sulphonamide resins are shown in the table given below.¹³³

Amide	Aldehyde	Composition of end-product	Nature of the end-product		
			Crystal- lizable	Resin Soluble and fusible	Insoluble and infusible
<i>o</i> -Toluene sulphonamide	CH_3O	$\text{R}\cdot\text{SO}_2 \quad \text{RSO}_2 \quad \text{RSO}_2$ $\text{HN}\cdot\text{CH}_2\text{-N-CH}_2\text{-N}\cdot\text{CH}_2\text{OH}$..	+	..
<i>p</i> -Toluene sulphonamide	"	" " "	..	+	..
<i>m</i> -Benzene disulphamide	"	$\text{C}_6\text{H}_4(\text{SO}_2\text{N}=\text{CH}_2)$ (polymer)	+
<i>p</i> -sulphamido benzamide	"	C_6H_4 $\left\{ \begin{array}{l} \text{SO}_2\cdot\text{N}=\text{CH}_2 \\ \text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{OH} \end{array} \right.$	+
Naphthalene-1- 3, 5 trisulphon- amide	"	$\text{C}_{10}\text{H}_7:(\text{SO}_2)_3(\text{N}\cdot\text{CH}_2)_2\text{NHCH}_2\text{OH}$	+
Aniline- <i>o</i> - sulphonamide	"	C_6H_4 $\left\{ \begin{array}{l} \text{SO}_2\cdot\text{N}:\text{CH}_2 \\ \text{N}:\text{CH}_2 \end{array} \right.$..	+	..
Aniline- <i>m</i> - sulphonamide	"	C_6H_4 $\left\{ \begin{array}{l} \text{SO}_2\text{N}:\text{CH}_2 \\ \text{NH}\cdot\text{CH}_2\text{OH} \end{array} \right.$	+
Aniline- <i>p</i> - sulphonamide	"	C_6H_4 $\left\{ \begin{array}{l} \text{SO}_2\text{N}\cdot\text{CH}_2 \\ \text{NHCH}_2\text{OH} \end{array} \right.$	+
"	CH_3CHO	C_6H_4 $\left\{ \begin{array}{l} \text{N}:\text{CH}\cdot\text{CH}_3 \\ \text{SO}_2\text{N}:\text{CH}\cdot\text{CH}_3 \end{array} \right.$	+
Aniline- <i>o</i> - sulphonamide	"	C_6H_4 $\left\{ \begin{array}{l} \text{N}:\text{CH}\cdot\text{CH}_3 \\ \text{SO}_2\cdot\text{NH}_2 \end{array} \right.$	+

Benzaldehyde condenses with aniline *o*-, *p*-sulphonamide to give benzylidene analogues, but an acetylated aniline sulphonamide gives no reaction with benzaldehyde:

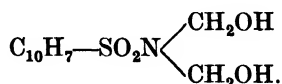


1-Methyl-4-amidobenzol-2-disulphonamide gives a crystalline compound with benzaldehyde,

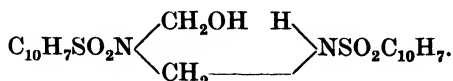


Aniline trisulphonamide gives no reaction with benzaldehyde.¹³³ Furfural condenses with aromatic sulphonamide containing in addition to one SO_2NH_2 group at least one substituted or unsubstituted SO_2NH_2 group. The products may be used for lacquers and moulded articles.¹³⁴

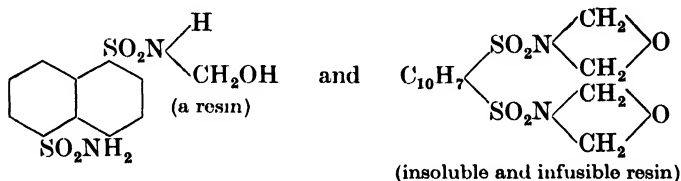
Naphthalene-1-monosulphonamide¹³⁵ with formaldehyde gives a crystalline compound, m.p. 120°, at low temperatures, which is a dimethylol compound, and is the first of its kind to be isolated:



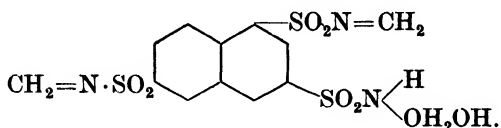
Condensation occurs on heating to give a resin



Naphthalene-1-5-disulphonamide condenses with formaldehyde in alkaline solution according to the scheme:



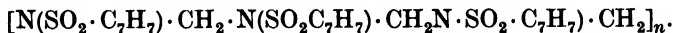
Naphthalene-1,3,6-trisulphonamide with formaldehyde in alkaline solution gives a resin transformable into an infusible form, probably



The above naphthalene resins show that the monosulphonamide varieties are not hardenable; the diamide varieties are hardenable on heating and the triamides are more easily hardenable.¹³⁶ Hexamethylene-tetramine with the above three give infusible resins. G. Walter and co-workers have also investigated (a) condensation products from amino-aryl sulphonamides with aldehydes, (b) naphthalene mono- and poly-sulphonamides, and discussed their thermo-hardening properties. It is quite possible that the reactions in the formation of these resins are similar to those which occur in the formation of the urea-formaldehyde resins.¹³⁷ Bren has found that urea and thio-urea improve the plastics derived from cellulose derivatives and sulphonamides.¹³⁸

A contribution by E. Hug¹³⁹ on the condensation of formaldehyde with aryl sulphonamides is of interest: *p*-toluene sulphonamide (1 mol.) and aqueous formaldehyde (1 mol.) at pH 7-9 give almost entirely *p*-C₆H₄Me·SO₂·NH·CH₂OH, m.p. 137°; β-naphthol affords dinaphthoxanthen and di-2-OH α-naphthyl-methane. The

resinous product obtained from the first condensation product with formaldehyde in an acid medium is considered to be:



p-Toluene sulphon-*o*-, -*m*-, and -*p*-nitroanilide, -*p*-toluide, and -*m*-4-xylylide do not react with formaldehyde.

The following toluene-sulphonamide-formaldehyde resins are used for lacquers:

Santolite, M.H.P. (Monsanto); a toluene-sulphonamide-formaldehyde condensation product; m.p. 55–82°, water-white in colour, s.g. 1.34–1.36; n_D 1.596; A.V. 0.02. It is soluble in acetone, benzene, and toluene (4:1); it is less soluble in alcohol.

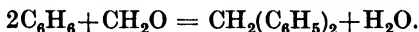
Gardilite is another name for Santolite. Santolite or Gardilite is insoluble in petroleum naphtha, soluble in strong alkalis, miscible with nitrocellulose and cellulose acetate, can be used as a coating for metals, and increases the adhesion and water resistance of cellulose acetate.

In the manufacture of safety glass toluene sulphonamide resins have proved invaluable, since they resist not only the action of ordinary light, but also ultra-violet light. The resin is compatible with nitrocellulose in a toluene butyl acetate solution. Toluene sulphonamide resins impart great adhesive properties to other films.¹⁴⁰ They are useful as plasticizers for acetyl cellulose or phenol-formaldehyde products, also for imparting water resistance to viscose threads by means of a solution of the resin in caustic soda. The water-resisting properties may be used for cold-water paints and for paper and for wood. In the near future there is no doubt that further work will be forthcoming, especially since sulphonamide resins possess remarkable water-resisting and insulating properties (*Brit. Plastics*, 1938, 493). W. H. Moss¹⁴¹ obtains resins by the interaction of an aryl sulphonamide, a halogen compound, e.g. amylene dichloride and a di-*p*-hydroxyphenyl compound, e.g. $\text{C}(\text{CH}_3)_2(\text{C}_6\text{H}_4\text{OH}-p)_2$. According to the molecular ratios of the reactants hard clear resins, compatible with cellulose acetate, or thermo-setting resins are produced. These confer anti-crease properties on textiles and may be fixed thereon by applying the reactants and heating to 130°. This is a novel form of a resin from a sulphonamide.

ALDEHYDE AND KETONE CONDENSATION RESINS

The aldehyde group alone, quite apart from unsaturated carbon atoms, is of sufficient importance as a resin-forming constituent to be considered more in detail. Aldehyde resins have long been known, such as the mixtures of condensation products of acetaldehyde produced by the action of alcoholic potash.¹⁴² Ciamician showed their physical similarity with the terpene resins, but their respective constitutions are different. Baeyer¹⁴³ investigated condensations of formaldehyde and salicyl-aldehyde with benzene, mesitylene, and

chloral under the influence of acid agents. The general tendency appeared to be in the direction of the formation of diaryl-methane derivatives, e.g. with benzene and formaldehyde the reaction was



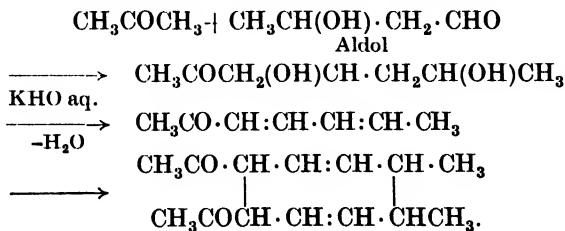
The product from mesitylene was



and from chloral $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{C}_6\text{H}_5 - \text{CCl}_3$.

L. Claisen and A. Claparède¹⁴⁴ dealt with the condensation of acetone, acetophenone, and benzaldehyde, acetone and furfural, using hydrochloric acid as condensing agent with benzaldehyde, and an alkali¹⁴⁵ with furfural. The results gave dibenzylidene acetone, benzylidene acetophenone, furfural acetone, all of which are crystalline products. Salicylaldehyde and acetone gave a resin. Ciamician and Silber¹⁴⁶ showed that benzaldehyde, not only in alcoholic solution, but without solvent, resinified in a sealed tube in sunlight without loss of hydrogen, giving a brittle yellow product, and showing four times the molecular weight of benzaldehyde.

Acetone forms solid condensation products with certain types of compounds: Werner¹⁴⁷ obtained an orange powder soluble in acetone and alcohol by the action of alkalis on acetone and formaldehyde; Miller¹⁴⁸ employed various alkalis as condensing agents. H. A. Gardner and C. A. Krauss¹⁴⁹ examined the condensation of aldehydes higher than formaldehyde: equimolecular quantities of acetone and aldol were refluxed with 10 per cent. caustic potash, until a liquid layer separated, which was neutralized with acetic acid and heated to 150° to drive off water. Furfural and aldol were the most promising, but paraldehyde did not condense. In order to impart hardness to the resin it was fused with rosin and then dissolved in acetone (1:1) to give a lacquer, whose durability was fair, compared with ester gum and damar, but the colour was darker. To prevent the formation of gummy products a resin was added directly to the reaction mixture and hydrochloric acid was used as a catalyst.



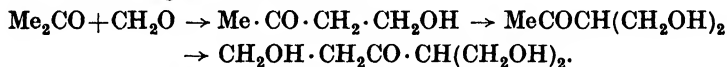
An attempt was made to produce a solid resin containing cellulose compounds which are themselves soluble in ketones and aldehydes. Acetone, aldol, and nitrocellulose solution was refluxed and hydrochloric acid gas passed in, rosin was added, and the mixture again refluxed. After driving off the excess of acetone a hard yellow mass

was obtained which gave a lacquer fairly light in colour and of good durability.¹⁴⁹

Carleton Ellis in America has protected by patents the conversion of acetone and formaldehyde by alkalis to give mouldable resins resembling horn, tortoise-shell, and ivory which are described in *British Plastics*, 1935, p. 568. Ivory products result when paraform is used, sodium phosphate being specified in one of the patents as condensing agent, while the syrupy intermediate product is treated with potash solution and taken up to 120° for conversions. In U.S. Patent No. 1,514,509 are given the steps necessary for the process, viz. the preparation of the syrup or gum, the cooling of syrup and catalyst solution and mould, the admixing and settling under refrigerating conditions to permit air-bubbles to escape, and warming in mould under carefully controlled temperature in order to avoid discoloration of the ivory product.

During the last few years the Du Pont de Nemours Company have been interested in acetone-formaldehyde resins, and in one of their patented processes the substances are allowed to react in the presence of urea or similar nitrogen compounds at 100°. If cellulose nitrate or acetate be first dissolved in the mixture the mass is converted into an infusible resin.

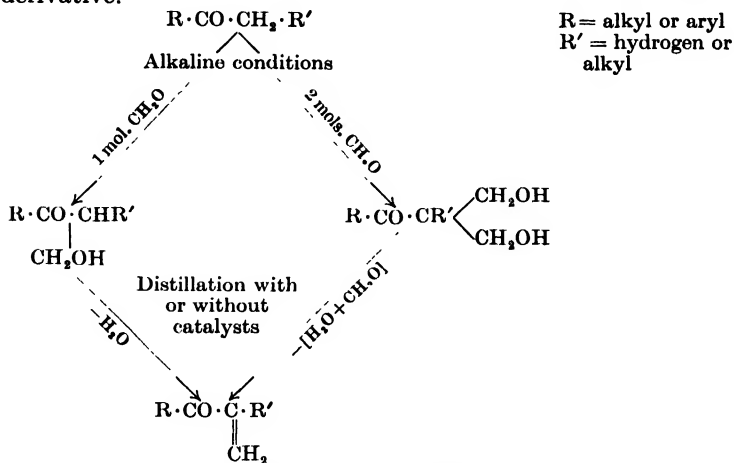
The condensation of acetone or methyl-ethyl ketone and formaldehyde takes place in the presence of a mild alkaline catalyst at 25°. The initial stages for acetone are:



The syrup gave on distillation *in vacuo* a colourless oil, b.p. 90–110°/16 mm. This oil polymerized spontaneously to a hard clear resin insoluble in organic solvents. Methyl-ethyl ketone gave under similar conditions a tough vitreous resin with excellent machining properties and a refractive index 1.52.¹⁵⁰

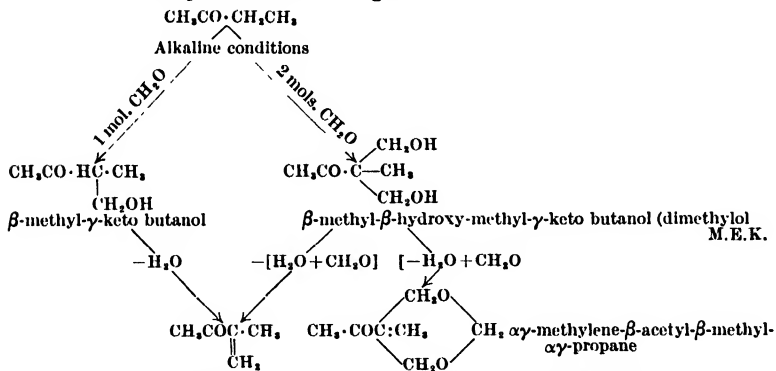
G. T. Morgan, N. J. L. Megson, and K. W. Pepper¹⁵¹ have examined colourless ketone-formaldehyde resins and they point out that at the present time the cost of glass substitutes, e.g. polymerides of methylacrylate, is high and the correction for chromatic aberration in moulded lenses is relatively limited. They have described the progress made with ketone resins, particularly those derived from methyl-ethyl ketone, which is as cheap as acetone, and its condensations are more easily controlled than those of its lower homologues. For comparative purposes a general account is given of the existing knowledge of other ketone condensations. The most promising products as substitutes for glass are those prepared under conditions represented in Scheme I (opposite). The saturated ketone-alcohols first produced may in some cases polymerize alone, but their value in resin formation lies in rapid dehydration to yield unsaturated methylene ketones. These vinyl or ethenoid derivatives are generally mobile liquids, which in sunlight and at room temperature polymerize spontaneously to colourless vitreous solids. The factors to be considered

are: (1) the optimum conditions of primary condensation to a ketonic alcohol; (2) dehydration of these keto-alcohols to unsaturated ketones, with purification and polymerization of the resulting vinyl derivative.



SCHEME I. Products of ketone-formaldehyde condensations

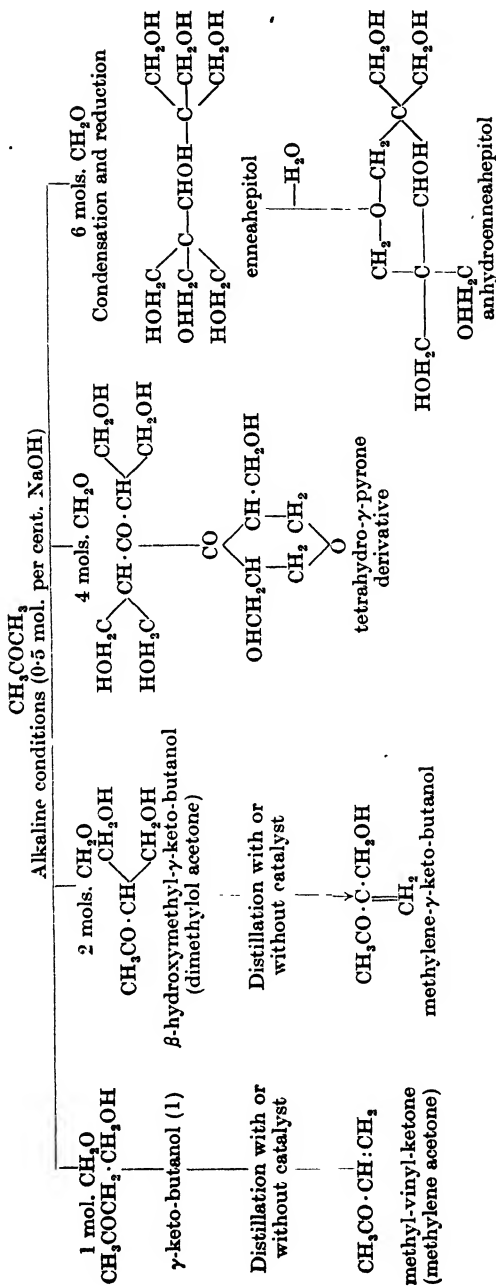
Methyl-ethyl-ketone-formaldehyde condensation may be represented according to the following Scheme II:



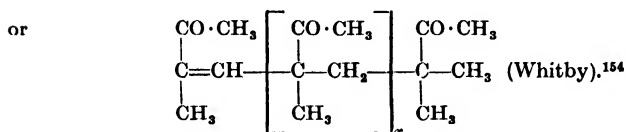
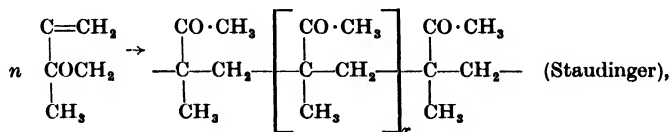
(XII) Methyl-isopropenyl-ketone (methylene M.E.K.)

SCHEME II. Methyl-ethyl ketone + CH₂O condensation

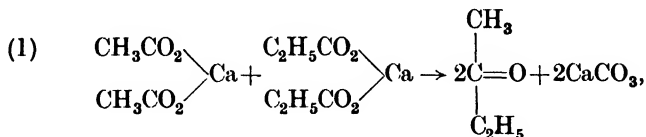
In Scheme III (p. 358) only the mono- and dimethylol types are of interest. Methyl vinyl ketone can be polymerized at 75° in the presence of benzoyl peroxide to give a resin with a refractive index 1.5, a softening-point of 60–70°, soluble only in ketones and esters. It may be used as an adhesive and in coating and impregnating compositions for paper and leather; moreover, it may be used as a moulding composition with wood, flour, and carbon black for gramophone records.



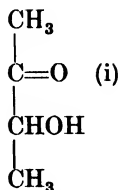
Methyl-isopropenyl ketone (methylene M.E.K.) polymerizes at room temperature with or without light to a hard colourless substance with brilliant lustre and may be ground or polished like optical glass. It may be used like methyl-vinyl ketone as a moulding powder, as an adhesive, and in impregnating conditions.¹⁵² Staudinger and R. Ritzenthaler¹⁵³ represent the polymerization as follows:



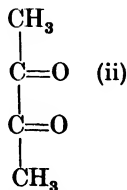
Methyl-propyl ketone, diethyl ketone, and acetophenone condensations with formaldehyde were also discussed, but methyl-ethyl ketone gave the most promising result which may lead to economical large-scale production. The general properties of methyl-ethyl ketone (M.E.K., butanone) are described by S. L. Langedijk,¹⁵⁵ who shows that it is an important component of acetone oil from Graukalk (techn. calcium acetate):



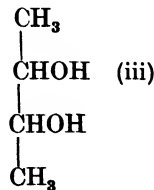
(2) Fermentation process:¹⁵⁶



(butanone-2-ol, 3)



(butanedione diacetyl)



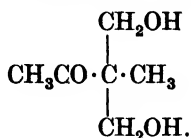
(butanediol 2-3;
2-3 buteneglycol)

(M.E.K. is obtained from (iii).)

(3) From *n*-butenes from cracked petrol gas \rightarrow alcohol \rightarrow butanone.¹⁵⁷

M.E.K. boils at 79.6° with normal chemical properties and on

condensation with formaldehyde gives 2-methyl-3 keto-butanol and a crystalline dimethylol compound of the formula



M.E.K. may be used in refining lubricating oils from wax and as a lacquer solvent for resins, nitrocellulose, and cellulose acetate.

The general study of the condensation of ketones and formaldehyde is of interest from technical and fundamental aspects.

Diacetone alcohol may be condensed with 3 mols. formaldehyde in the presence of alkali or an alkaline earth hydroxide or a soluble carbonate or phosphate.¹⁵⁸ Distillers Company, J. V. Eyre, and H. Langwell¹⁵⁹ have produced a resin of limited molecular complexity by the condensation of aldol in aqueous solution kept alkaline to phenolphthalein; with acetaldol as material an approximately C 12 compound is produced.

Resinification of Glycerol. S. N. Ushakov and E. M. Obriadina¹⁶⁰ describe new methods to obtain resin-like products from glycerol by heating with a catalyst. Good catalysts for the reaction are found to be easily reduced metallic sulphates; the best catalysts are mercurous and copper sulphates. The product has no independent technical importance, but it gives elasticity to phenol resins of the 'resole' or 'novolak' type, without depriving them of their primary properties. Glycerol resins should be useful for the preparation of protective coatings (resistant to acids and alkalis) where elasticity is of importance. Glycerol resins can be used as plasticizers for the preparation of plastic masses of an albumin base (casein, albumin, leather plastics).

With the increasing economic importance of artificial rubber the role of glycerol as a raw material becomes more and more significant. Glycerol, gluten, turpentine, and sulphuric acid all react on heating to give a rubber-like elastic composition which can be vulcanized to any degree of hardness and toughness.¹⁶⁰

CYCLOHEXANONE RESINS

Cyclohexanol is the product of hydrogenation of phenol at 160–200° under 4 atmospheres pressure with nickel as catalyst; similarly, methyl-cyclohexanol can be obtained from cresol. Cyclohexanone is produced by the dehydrogenation of cyclohexanol or by the action of a hydrogenating catalyst on a phenol, cyclohexanol mixture, and oxidation of the product with bichromate. Cyclohexanol as a solvent is known as hexalin, anol, hydralin, and adronal; HA solvent as hexalin-acetate; methyl-cyclohexanol as methyl-adronal, methyl-anol, sextol, and methyl-hexalin; cyclohexanone as sextone, anon, and hexanon.

Cyclohexanol or its methyl derivative has been condensed with phthalic acid, a resin acid, and glycerol. It has been condensed with styrene and acetic anhydride to give colourless masses suitable for moulding.¹⁶¹

Cyclic ketones, e.g. cyclohexanone and cyclohexyliden-cyclohexanone, are transformed into resinous condensation products by heating with alkalis. Cyclohexanone with alcoholic potash under pressure at 200–20° gives a resin which is soluble in alcohol, benzene, cyclohexanone, and linseed oil.¹⁶² By condensation of cyclohexanone with acids (50 per cent. sulphuric acid) or substances like zinc chloride, resins are obtained which are with difficulty soluble in alcohol, but soluble in benzene and linseed oil.¹⁶³ Condensation of acetaldehyde and cyclohexanone (or homologues) occurs by heating the components in the presence of acids or basic condensation materials with or without addition of solvents (alcohol, benzene). After the alcohol is distilled off there remains an oil which gradually passes into a solid resin. Cyclohexanone and its derivatives give good soluble resins. It is of advantage to use alkaline or acid condensation agents and to carry out the reaction under pressure.¹⁶⁴ Cyclohexanone reacts with formaldehyde (equimolecular amounts) in the presence of acids (sulphuric acid) or bases (caustic soda) by heating, with the formation of a resin, which is washed, dried, and heated at 130–35° until when tested on cooling it is hard and transparent.¹⁶⁵ The product is soluble in alcohol, ether, acetone, chloroform, benzene, and easily in cyclohexanone. The resins have high lustre and transparency and good stability to light and are quite free from smell. O. Schmidt and K. Seydel claim a resin for varnishes by condensing cyclohexanone, formaldehyde, and rosin.¹⁶⁶ According to C. Ellis,¹⁶⁷ colourless resins are obtained by the use of mild alkalis and anhydrous formaldehyde. A cyclohexanone resin becomes insoluble on continued warming. In place of cyclohexanone, methyl-cyclohexanone may be used. J. and G. Baer¹⁶⁸ obtain a solid resin (colourless and soluble in organic solvents) by condensation of cyclohexanone and aqueous formaldehyde with aqueous soda without external heating. Phenols may be mixed with cyclohexanone and formaldehyde to give resins suitable for use with nitrocellulose of low viscosity.¹⁶⁹ Mixtures of cyclohexanone and phenols may be made to react with aldehydes of different kinds to produce manifold resin products which are soluble in linseed oil.¹⁷⁰ The Bad. A.S.F. in Germany and Ellis in America have shown great interest in these cyclohexanone forms of resins, anhydrous formaldehyde being used to give colourless products. In the German specifications the resins are colourless, odourless, readily soluble in linseed oil and compatible with phenol-formaldehyde resins. Cyclohexanone may be made to condense with polymerized vinyl acetate in the presence of an acid condensation catalyst, e.g. sulphuric acid, to give insoluble condensation products for use in making lacquer, moulding compositions, &c. A cyclic ketone, e.g. a methyl-cyclohexanone or *p*-chloro-cyclohexanone, may be used.¹⁷¹

A resin of the type cyclohexanone vinyl, melts between 100° and 120°, has a low acid value, and is soluble in nitrocellulose solvents and drying-oils (requires heating to 250°). It is insoluble in alcohol; suitable for nitrocellulose and cellulose ether lacquers and oil varnishes; but it is not suitable for straight tung-oil varnishes or cellulose-acetate lacquers.

From α - and β -naphthols and cyclohexanone in the presence of zinc chloride complicated resins of an oxidizable character may be obtained.¹⁷² Crystalline cyclohexyl-naphthols are recognizable as components. Phenols, including cyclohexanone, hydroxyl derivatives of pyridine, chlorinated phenol, or phenol-sulphonic acids in liquid phase, react with acetylene at 300° in the presence of zinc or cadmium to give resins.¹⁷³

A review of the properties of cyclohexanone resins is given in *British Plastics*, 1938, p. 607.

POLYAMIDES

The polymerization of hydroxyacids is discussed in Chapter XVI, p. 473, and it is shown that similar condensation polymers are obtainable from amino-acids. The polyamides are closely related in structure to natural proteins, and certain polyamides can be spun into fibres. Just as in the case of the hydroxyacids, the super-polymers of the polyamides form the basis of the synthetic fibres of the Nylon class and have important and increasingly widespread application in the textile industry, &c., in competition with viscose, rayon, and possibly also silk. Nylon fibres have a strength about $1\frac{1}{2}$ times that of silk and over twice as great as ordinary rayon when dry or 4 times as strong as rayon wet, and is superior to both silk and rayon in combined strength and elasticity. Rayon will not replace silk in making sheer hosiery. Nylon is characterized by a high degree of 'crimp' recovery, especially after the knitted garment has been set by steam, and in this respect is as good as silk. Nylon hosiery may be expected to be equal to that of semi-service silk. It is less absorbent than silk to water, but it lacks the soft luxurious 'handle' and is said to have a cold feel. According to Warrington, most of the other uses of Nylon are prospective rather than actual. At present many of the developments await the time when Nylon yarn and polymers are more freely available.

A short description of the polyamide class of resins is given in Chapter XVI, p. 475.

HYDROCARBON ALDEHYDE RESINS

Many hydrocarbons containing neither acidic nor basic groups can be made to react with formaldehyde in such a way as to give a resin which is of the oil-soluble class (cf. petroleum hydrocarbon resins, Chap. XII). Naphthalene condenses with formaldehyde in the presence of sulphuric acid. Grabowski¹⁷⁴ showed that naphthalene gave

dinaphthyl-methane when 5 parts of naphthalene reacted with one part of formaldehyde in 20 parts of chloroform, using 10 parts of concentrated sulphuric acid as a condensing agent. Other aldehydes behave similarly. This reaction has been employed in removing aromatics from cracking-oil tars (cf. p. 319). Wheeler and Jackson¹⁷⁵ obtained a resinous product from formaldehyde and naphthalene. The Badische Company, some years later, described conditions for producing such resins.¹⁷⁶ Improvements in manufacture were subsequently introduced.¹⁷⁷ A comparison of the processes may be made by reference to the details arranged in the table.

Table showing the Comparative Methods of Producing Naphthalene Resins

	Folchi	Bad. Anil. Soda F.	Vingtrie	Bayer
Napthalene (parts)	100	100	100	100
Formaldehyde (parts)	24	24	40	22
Formaldehyde (mols)	1	1	2	1
Water (parts)	56	56	260	31
Temperature	70-80°	110°	140°	110°
Yield (parts)	100-10	..	(autoclave)

Time of reaction, about 2 hours; drying time, several hours.

The molten resin when prepared is well washed with water, alkali, and finally with water again and dried at 80° for several hours. The light-yellow resin is water-resistant and insoluble in alcohol. It is soluble in benzene and turpentine. It is brittle and requires addition of drying-oil to give it elasticity in use as a varnish or lacquer. Certain difficulties associated with the washing of the resin and preservation of its light colour have been overcome to some extent in later processes protected by Meister, Lucius, and Brüning.¹⁷⁸ Resins *soluble* in linseed oil have been obtained from naphthalene and other aromatic hydrocarbons and their derivatives by condensing in acetic acid as a solvent, using phosphoric acid, halogen acids, or sulphuric acid as catalysts.¹⁷⁹ Acid-reacting salts such as zinc chloride and tin chloride have also been used as condensing agents.¹⁸⁰ Chlorinated naphthalene and hydrogenated naphthalene (tetralin) can be resinated in this way.¹⁸¹

RESINS FROM AROMATIC NAPHTHAS

A use for solvent naphtha is suggested in a patent of the I.G. Farbenindustrie, A.G.¹⁸² The proposal is to condense solvent naphtha, preferably free from phenols and bases, with a *m*-alkyl-substituted phenyl-alkyl-ether; the alkyl substituent in the phenyl groups may be the same as, or different from, that in the ether groups and a second *m*-alkyl-substituent may also be present (i.e. in a 3-5-dialkyl-phenyl-alkyl-ether). The products are completely soluble

in drying-oils. If the *m*-substituted ethers are replaced completely by the corresponding *o*- or *p*-substituted ethers the products are always completely or mainly insoluble in aliphatic or hydro-aromatic petroleum. The properties of the resins as to solubility, melting-point, and colour are governed to a large extent by the nature of the catalyst used. With tin tetrachloride very light-coloured resins, insoluble in polymerized oils, but soluble in drying-oils, are obtained; the use of borofluoroacetic acid leads to a nearly colourless high-melting resin soluble in polymerized oils, whereas when sulphuric acid is used as a catalyst, lower-melting resins, light-brown in colour and soluble in polymerized oil, are produced. The resins are suitable bases for the manufacture of oil lacquers and plastic masses; they can be worked up with cellulose esters to completely transparent, highly lustrous drying-mixtures.

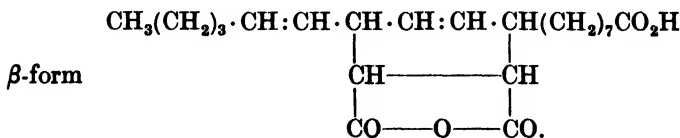
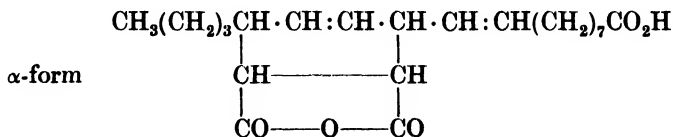
Many miscellaneous resins are difficult to group under appropriate headings, and it is feared that a number have been omitted. Examples of this difficulty may be given in the following cases:

(1) *Resins from Unsaturated Hydrocarbons with Unsaturated Ketones.*¹⁶⁶

Mono- or poly-olefine benzenes or naphthalenes, e.g. styrene, divinyl benzene, vinyl-naphthalenes, polymerize with unsaturated ketones containing an olefine linkage in conjugation with the keto-group, e.g. vinyl-methyl ketone, methylene-ethyl-methyl ketone, or benzal acetone, by simple heating or by emulsion with water and an emulsifying agent. Among the examples given is the polymerization of vinyl-methyl ketone and styrene at 80° for 8 days. Vinyl naphthalene alone is polymerized in ethyl benzene solution by heating at 100–20° with benzoyl peroxide or stannic chloride as catalyst to give a tough lacquer from toluene or xylene solution.¹⁶³

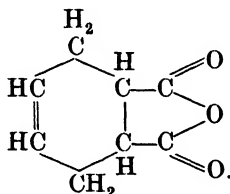
(2) *Resins obtained by the Diene Synthesis.*

(a) *Maleic anhydride compounds of doubly conjugated glycerides of α - and β -elaeostearin.* Morrell and Samuels¹⁶⁴ showed that maleic anhydride combines with α - and β -elaeostearic acids to form compounds of the structural formulae:



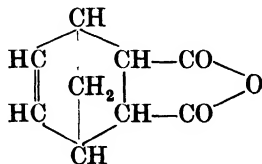
The anhydride combines with the corresponding glycerides at 75° exothermally to give viscous compounds.¹⁸⁵ The β -compounds thermo-harden on stoving to give films which may be used as varnishes (cf. Chap. XI, p. 296). The corresponding α -compounds do not stove readily and do not thermo-harden. The difference in behaviour of the two substances is attributed to the position of the chain double linkage. The partial esterification of the maleic anhydride by glycol or glycerol increases the viscosity of the compounds and confers durability to the films. Previous heat-thickening of the β -elaeostearin before combination with maleic anhydride gives a more durable varnish. The study of the maleic anhydride compounds of α - and β -elaeostearic acids and of their glycerides has thrown light on the changes which take place during the drying of unsaturated vegetable oils. Some of the defects of drying-oil films may be traced to changes which occur in the peroxides formed on oxidation.¹⁸⁶

(b) Brooks and Cardarelli¹⁸⁷ have utilized the reaction between butadiene and maleic anhydride to form a dibasic acid or anhydride of the following structure:



This product reacts with glycerol, polyglycerol, and polyglycols to form resins. The butadiene employed is obtained from the products of the vapour phase cracking petroleum.

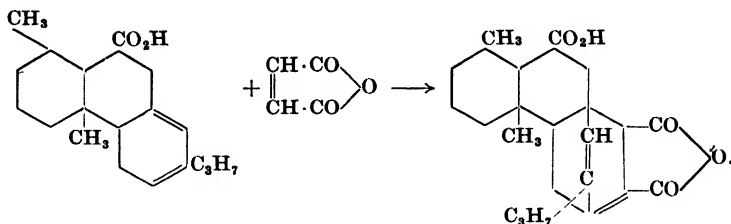
In this connexion it should be noted that the diene reaction with maleic anhydride has been employed in the purification of crude benzene to remove cyclopentadiene. The product of the reaction is as shown:



(methylene tetrahydrophthalic anhydride).

(c) Among the additions to the resinous substances formed by the Diels-Alder reaction may be mentioned (1) Alresate (177 c, 201 c, 313 c, Dr. K. Albert, G.m.b.H.) which are abietic acid, maleic anhydride products compatible with drying-oils to give varnishes.

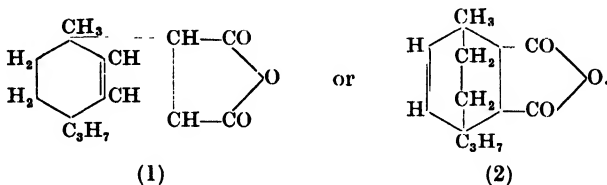
According to Ruzicka the substance would be represented by the formula:



Alresate 313 c has an acid value of 15 and melts at 95–105°. Methyl abietate and maleic anhydride form a compound which can be refluxed without decomposition, m.p. over 100°. It is of light colour and does not yellow on exposure (cf. Chapter XVII, p. 523).

(2) Petrex, a diene product from certain terpinoid substances— α -terpinene, dipentene, α -terpineol, or terpin hydrate.

From α -terpinene a substance of the following formulæ¹⁸⁸ is obtained:



The second formula represents an endo-ethylene compound of tetrahydrophthalic acid. In addition to the above, polymerized products are obtained with ratios of hydrocarbon to maleic anhydride 2:1 and 3:2. They are compatible with drying-oils and are resistant to alkalis and the action of alcohol, which may be due to their structure under formula (2). Their glycol esters are harder than those of phthalic anhydride and in that respect may be compared with the glycol esters of the β -elaestearin compound previously described. The terpinene residue acts accelerating in conjunction with the usual 'driers' on film formation. Hercules Powder Co.¹⁸⁹ condense dipentene, maleic anhydride, and rosin or abietic acid at 200°. The product may be esterified by glycerol at 200–50°, and drying-oils or their acids may be incorporated during the esterification. D. G. Anderson and R. L. Yeates¹⁹⁰ condense maleic anhydride, an unsaturated acid (linseed-oil acids), and cyclohexanol at 220–5° to give thermo-hardening resins compatible with nitrocellulose (cf. Chapter XI, p. 304).

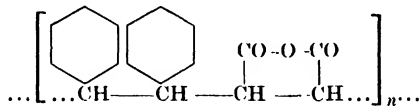
When aconitic acid ($\text{HO}_2\text{CH}:\text{C}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$) is condensed with a terpene or terpene alcohol, the resulting resin is dark in colour and unsuitable as a varnish ingredient. A pale resin can be obtained from citric acid, which changes readily to aconitic acid when heated

with a mineral acid, turpentine oil, blown linseed oil, and linoleic acid, and subsequent esterification with glycerine.¹⁹⁰

(d) *Additive polymers.* An interesting type of polymer described by Wagner-Juaregg¹⁹¹ is produced by the reaction of stilbene with maleic anhydride. These two substances are allowed to react in boiling xylene and an amorphous additive results. The progress of polymerization is not uniform; hence a mixture of polymers is obtained. About 10 per cent. are sufficiently soluble in camphor to allow a molecular weight to be taken. Wagner-Juaregg found the mean molecular weight of the soluble portion to be 4,200, equivalent to a polymer of 15 unit molecules.

The insoluble portion has unquestionably a higher molecular weight.

In this additive hetero-polymerization (Wagner-Juaregg) a curious stoichiometrical relationship appears. The combination of maleic anhydride takes place molecule by molecule and the chain is supposed to be formed of alternate units of stilbene and maleic anhydride, the structure being represented as follows:



It matters not whether an excess of stilbene or maleic anhydride be present, the molecular combining ratio being approximately 1:1. The additive polymer behaves as a saturated compound, absorption of bromine being negligible.

A number of resinous products involving the production of such polymers have been prepared:¹⁹² maleic anhydride, for example, being allowed to react with such hydrocarbons as styrene, vinyl acetate, indene, and various others. One product is made by the reaction of a mixture of styrene, vinyl acetate, and maleic anhydride in acetone as solvent medium. Heat is applied and the heat treatment is continued until the viscosity no longer increases, indicating the completion of the polymerization. The acetone is removed by distillation *in vacuo*, leaving a colourless hard, elastic mass of resin. It is the opinion of Carleton Ellis¹⁹³ that polymerization with mixed reagents to produce additive polymers is destined to provide a number of coating agents of utility.

This should prove the case especially when products are required of a particular type not easily obtained by homo-polymerization. The processes of additive polymerization are an inviting field of investigation.

Substances of similar type have been obtained from certain highly unsaturated fish oils containing no conjugated double linkages, by combination with maleic anhydride.¹⁹⁴

(3) *Pentaerythritol Resins.*

Pentaerythritol yields valuable products by condensation with polybasic saturated or unsaturated fatty acids and resin acids; also

with alkyl halides or ethers; they can be used as solvents, plasticizers, and resins. At higher temperatures they become insoluble, infusible substances and may be colourless or brightly coloured. The products from pentaerythritol and the higher mono-basic fatty acids or resin acids have other valuable properties, e.g. erythritol, linseed oil, rosin, and small amounts of boric acid heated in an autoclave at 220–50° and then blown in the presence of 1 per cent. lead manganate at 60–80°, give a product adapted to interior and exterior use, which can be compounded with lakes, fillers, &c., and shows good drying properties.¹⁹⁵

(4) *Polymerized Alkylene Oxides.*

When the vapour of an alkylene oxide, e.g. ethylene or propylene oxide, is passed over catalysts at temperatures above 100° products of various degrees of polymerization are obtained, ranging from wax-like materials of a solid or semi-solid nature to other polymers of a more fibrous character. The usual catalyst is an alkaline substance, e.g. NaOH or KOH, although under some conditions catalysts of an acid character have been recommended.¹⁹⁶ These polymerized oxides are proposed for use in coating compositions along with cellulose esters or ethers, the softer polymerization products being utilized as plasticizers for nitrocellulose. Fusible resins are obtained by treating the condensation products from phenols and aldehydes with alkylene oxides at high temperature.

The polymerization of alkylene oxides is discussed in Chapter XVI, p. 450.

(5) *Condensation of Polyhydroxybenzenes and Ketones.*

Non-yellowing resinous compositions are obtained by the condensation of polyhydroxybenzenes and ketones with an acid catalyst, e.g. resorcinol and acetone with HCl aq. on heating to boiling for 2 hours yield a brittle opaque resin; moreover, mesityl oxide ($\text{CH}_3\text{—CO—CH=C}(\text{CH}_3)_2$) with resorcinol gives a resin which is soluble in vegetable oils.¹⁹⁷

(6) *Phenol Ether Resins.*

Oil-soluble resins can be obtained by condensation of aldehydes with alkyl ethers of aromatic compounds.¹⁹⁷ Tertiary-butyl phenyl ether, tertiary-amyl phenyl ether, and other tertiary and secondary alkyl phenyl ethers are proposed. These resins can be used in conjunction with the usual phenol- and cresol-aldehyde resins and are suitable for the preparation of varnishes, lacquers, and enamels for coating metal, paper, &c. A mixture of butyl-phenyl-ether and *p*-tertiary butyl phenol is stated to be produced when cresol and tertiary butyl alcohol are condensed by sulphuric acid; both the ether and the substituted phenol are reactive to formaldehyde and yield oil-soluble resins. In order to avoid sulphonation alkaline condensing agents may be used, e.g. caustic soda. For the reaction with

formaldehyde, using NH_4OH or sodium acetate¹⁹⁹ as catalysts, it is not known to what extent and in what manner rearrangement of ether to substituted phenol takes place. The resins possess chemical stability, pale colour, and are free from uncombined phenol; they are insoluble in alkalis, retain their pale colour when heated, and are permanently fusible at higher temperatures. While a large number of phenols, e.g. 4-hydroxy-1:3 dimethyl benzene, other xylenols, and phenyl phenol, may be used, yet it is essential that at least one reactive position in the phenol or the ether should be unoccupied. Phenol ethers can be made also by interaction of phenols and unsaturated compounds, e.g. those produced in petroleum cracking (p. 319), e.g. cresylic acid and amylene with concentrated sulphuric acid yield amyl-phenyl-ethers and substituted phenols which can be condensed with CH_2O to give transparent resins soluble in varnish oils.

(7) *Resins from Carbohydrates.*

F. M. Hesse²⁰⁰ has described the properties of many of the carbohydrate products. In view of the aldehyde-alcohol character of these substances reaction with phenol or aniline, urea or formaldehyde, is to be anticipated. Sucrose will condense with either phenol or aniline to give black brittle materials which can be used in moulding mixtures. With formaldehyde or with urea products may be made resembling glass.²⁰¹ A thermo-hardening resin can be made from a saccharide, formaldehyde, and aliphatic acids, e.g. tartaric or succinic acid,²⁰² but combination of a hexose with maleic anhydride gives a water-soluble resin.²⁰³

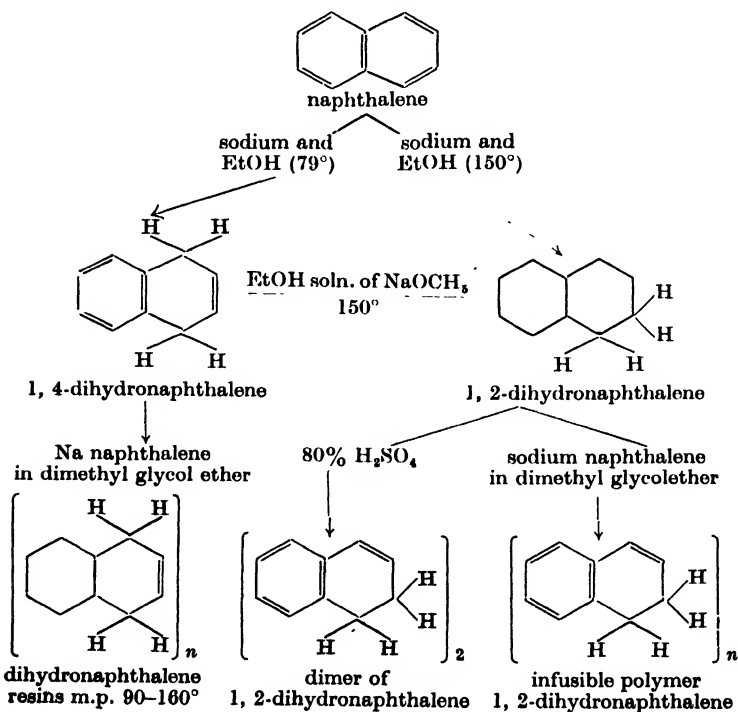
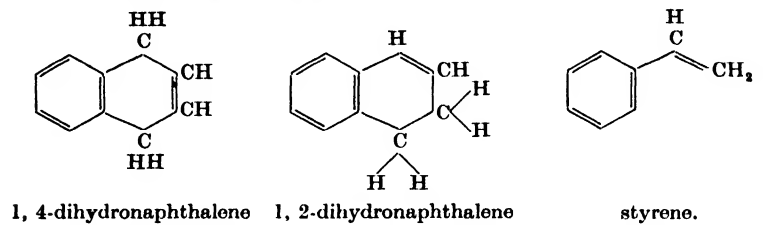
Exploration in the field of sugar plastics has begun during the last few years, especially in the direction of finding another outlet for Cuban sugar and molasses. According to Hesse (loc. cit.) the final product obtained from phenol and sucrose is, after moulding, claimed to be equal to, if not better than, any product of its kind on the market. It is, however, admitted that up to the present time the manufacture has been done on a laboratory scale or on a semi-industrial scale in the case of sucrose-phenol resins. From sucrose-formaldehyde and urea it is claimed that a glass may be produced which will be more elastic than ordinary glass and will not splinter. Here again the process is not yet fully developed. It is evident that this new class of plastics will demand attention, but it is not anticipated that it will be used for varnish coatings.

(8) *Dihydronaphthalene Resins.*

A series of new hydrocarbon polymers has been provided by the polymerization of isomeric dihydronaphthalenes with sodium naphthalene. From 1, 4-dihydronaphthalene light-coloured thermoplastic resins are obtained. From 1, 4-dihydronaphthalene are produced infusible polymers, which, although completely insoluble in most solvents, will form colloidal solutions in some halogenated aromatics.

By the action of 80 per cent. sulphuric acid on 1, 2-dihydronaphthalene it is converted into a mixture of dihydronaphthalene dimers. 1, 4-dihydronaphthalene is conveniently prepared by the reduction of naphthalene with sodium and alcohol; it may also be produced by the hydrolysis of sodium naphthalene. This isomer is rearranged to 1, 2-dihydronaphthalene by the action of sodium ethylate.²⁰⁴

The following schemes will show the comparison of the structural formulae of these substances with styrene and also the interrelation of dihydronaphthalene products.



The resins obtained from the 1, 4-compounds are brittle, glass-like solids with density 1.14; soluble in benzene or turpentine, and

compatible with vegetable oils. They darken slightly on heating in air, but will stand 370–450°.

Dimerization of the 1, 2-isomer by sulphuric acid gives a viscous liquid (b.p. 235° at 15 mm.), which on standing gives a crystalline substance, m.p. 51, but on treatment with sodium naphthalene does not cause further polymerization. The infusible 1, 2-polymer forms a colloid solution in halogenated aromatics, and on heating the polymer swells and dissolves to form a syrupy solution which sets to a gel on being cooled. The polymerization of 1, 2-dihydronaphthalene is a definite catalytic process, but the polymerization of the 1, 4-isomer appears to have a more complicated mechanism.

Although the practical application of these polymers has not been explored, the study of their polymerization in comparison with that of styrene is of considerable interest.

The I.G. Farbenindustrie, A.-G.,²⁰⁵ use a tetrahydronaphthalene derivative containing one or more halogen methyl groups in the β -position, which is heated with a polynuclear aromatic or hydroaromatic compound; e.g. 6-chloromethyl, 1, 2, 3, 4-tetrahydronaphthalene heated with naphthalene until HCl is produced yields a resin soluble in benzene or petroleum; tetralin may be used instead of naphthalene to give an oil-soluble resin.

(9) *Emulsion Resins.*

Reference has been made in the previous chapter to direct or emulsion polymerization of butadiene in the manufacture of Buna. Diene polymerization may be carried out either in bulk or emulsion form. Earlier work was based on bulk polymerization by the aid of slightly elevated temperature only, a slow process and difficult to control. Methyl rubber was made by this method. The first Buna rubber was made by bulk polymerization of butadiene as promoter, the name being derived from Bu (butadiene) and Na (sodium). This was a slow process and was abandoned for the emulsion method. In the emulsion technique the ingredients are emulsified with water with an emulsifying agent and subjected to conditions of temperature and pressure suitable for converting them into a suspension of synthetic resins which resembles the latex obtained from the rubber tree. Compared with older methods the polymerization proceeds rapidly, although the process requires close control; it does not present, however, any problems that differ greatly from those ordinarily met with in chemical manufacturing operations. Recovery of the synthetic rubber from the emulsion is similar to the recovery of natural rubber from latex.²⁰⁶ Recently cyano-butadiene and butadiene or chlorobutadiene have been polymerized in aqueous dispersion with sodium oleate as emulsifier²⁰⁷ to form an emulsion of synthetic rubber, somewhat similar to rubber latex and with satisfactory results. Salts of isopropyl naphthalene sulphonic acid may be used as emulsifiers.²⁰⁸ The emulsion polymerization of acrylic acid resins has been also investigated and also co-polymerization of a maleic ester and vinyl chloride.²⁰⁹

In the two cases mentioned below the resin (already formed) is dissolved in a suitable solvent which is emulsified, and the separated resin is adsorbed by a fibrous filler. They differ in that respect from the emulsion polymerization process employed in the manufacture of Buna.

L. Robin and M. van Roggen²¹⁰ claim the use of synthetic resins (phenol- or urea-formaldehyde, alkyds, &c.) dissolved in a solvent, e.g. EtOH, in which is dissolved a product such as a soap or saponifying agent, which is substantially insoluble in the resin and to which a plasticizing solvent (furfuraldehyde) is preferably added. The solution is dispersed by, e.g., water, which dissolves the solvent and added product, but not the resin, and in which a fibrous filler is suspended. The colloidal resin and filler are separated and the product is moulded to form automobile body parts; the moulding pressures are low. *Peton*²¹¹ is fibre impregnated with an emulsified synthetic resin (phenol- or urea-formaldehyde, alkyds, &c.) for nuts, bolts, gear-wheels, &c.

PROPIOLIC ACID RESINS

Reference has been made under acrylic acid resins to the preparation of propiolic acid ($\text{CH}=\text{C}\cdot\text{CO}_2\text{H}$) from acetylene. The new methods have stimulated interest in the potential uses of this reactive acid. According to DuPont de Nemours & Co.,²¹⁰ the acid condenses with hydroxy-compounds under certain conditions to form products of interest for the varnish and plastics industries, e.g. with ethylene glycol, glycerol, and pentaerythritol, and especially with sugars and polyvinyl alcohol. With ethylene glycol a water-soluble viscous oil is formed, rendered insoluble and tough by continued heating. With pentaerythritol a tough and leathery product is obtained, which is insoluble in water and most organic solvents. Essential conditions for the formation of resinous masses include heating of the mixed components for several days at 110° . With cane sugar a black stiff tar is obtained, but a resin resembling hard lac can be isolated by extracting with formamide and treatment of the formamide solution with water. The resin does not fuse at 240° . A modified drying-oil can be obtained by heating glycerol, propiolic acid, and linseed oil which is stated to surpass linseed oil in baking and drying properties.

REFERENCES

1. *Helv. Chim. Acta*, 1935, 18, 491; B., 1935, 734; R. Houwink, *Elasticity, Plasticity and Structure of Matter*, 1937.
2. *Rev. Chim. Ind.*, 1926, 35, 365.
3. Bühler, G.P. 334,984 and 335,014 (1917).
4. G.P. 613,284; *Chem.-Tech. Übersicht*, 1935, 59, 107.
5. F.P. 612,306.
6. F. Seebach, U.S.P. 1,693,701.
7. Haller and Kappeler, B.P. 266,358 and 274,501.
8. *Oester. Chem. Ztg.*, 1921, 16.
9. G.P. 305,026.
10. B.P. 404,469; B., 1934, 244.

11. B.P. 401,535; 401,965; 405,491; 415,555; B., 1934, 972; U.S.P. 1,999,069.
12. International Gen. Electric Company, B.P. 399,738; 414,293; B., 1934, 941.
13. U.S.P. 1,999,069.
14. B.P. 432,143; B., 1935, 861, and H. Rauch, G.P. 401,726 (1922).
15. *Brit. Plastics*, 1931, 3, 262, and 1935, 6, 356.
16. Swiss P. 165,840 (1934).
17. U.S.P. 1,940,383; B., 1934, 849.
18. U.S.P. 1,930,601 (1934); 1,969,744; 1,999,093; B.P. 343,031; B., 1931, 503.
19. B.P. 402,050 (1933).
20. B.P. 424,536 (1934); B., 1935, 368.
21. H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *J. Amer. Chem. Soc.*, 1933, 55, 4571.
22. B.P. 486,611; B., 1939, 177.
23. B.P. 478,370; B., 1938, 1196.
24. B.P. 482,120; B., 1938, 602; B.P. 495,514; B., 1939, 177.
25. *J.S.C.I.*, 1935, 54, 17, and G. T. Morgan, *Chem. Ind.*, 1937, 103.
26. *Angew. Chem.*, 1939, 62, 215; B., 1939, 629; and *Chem. Age*, 1941, 44, 95.
27. *Ind. Eng. Chem.*, 1941, 33, 1203.
28. *Ibid.*, 1928, 20, 597.
29. G. Kranzlein, *Aluminium Chloride in der organischen Chemie*, 1932.
30. F. H. Groggins, *Chem. Met. Eng.*, 1927, 34, 291.
31. Anon., *Chem. Trades J.*, 1932, 443.
32. Anon., *Syn. App. Fin.*, 1933, 25, 1211.
33. *Ind. Eng. Chem.*, 1933, 25, 1211.
34. G. A. Bennett, C. K. Drinker, and M. F. Warren, *J. Ind. Hyg.*, 1938, 20, 97.
35. B.P. 450,578.
36. B.P. 488,110.
37. Bad. Anil. Soda Fabrik, G.P. 280,377; 280,595 (1913); and 326,729.
38. Farb. Meister, Lucius u. Brüning, G.P. 417,442; B., 1926, 100, 203.
39. Farbenfabr. vorm. Fr. Bayer & Co., G.P. 302,531 (1916).
40. G.P. 336,476 (1918).
41. Farb. M. L. u. Brüning, G.P. 400,312; B., 1925, 216.
42. I.G. Farbenind., A.-G., G.P. 436,681 and 446,999 (1928).
43. Bad. A.S.F., G.P. 326,729 (1913).
44. B.P. 407,948 (1934).
45. Farb. M. L. u. Brüning, B.P. 240,318; B., 1925, 965.
46. C. H. Penning, *Ind. Eng. Chem.*, 1930, 22, 1180.
47. A. W. van Heuckeroth and H. A. Gardner, A.P.V.M., *Circs.* 369 and 430.
48. *Paint Techn.*, 1936, 1, 401,441; 1937, 2, 25; B., 1937, 590.
49. R. L. Jenkins, Swan Res. Inc., U.S.P. 1,974,801.
50. G. M. Kline, *Ind. Eng. Chem.*, 1935, 27, 506.
51. U.S.P. 2,047,146; B., 1937, 1240.
52. I.G. Farbenind., F.P. 775,061.
53. B.P. 430,121.
54. B.P. 413,596; B., 1934, 847.
55. *J. Franklin Inst.*, 1933, 216, 635.
56. L. Light, B.P. 397,773; B., 1933, 929.
57. U.S.P. 1,960,266; B., 1935, 354.
58. A. V. Blom, *Farben-Chem.*, 1933, 4, 245.
59. L. Light, B.P. 397,773 (1933).
60. H. A. Gardner, B.P. 351,637 (1931).
61. A. Foulon, *Farbe u. Lack*, 1933, 358.
62. *Ind. Eng. Chem.*, 1930, 22, 31.
63. *Rec. trav. chim.*, 1934, 53, 359; A., 1934, 518.
64. F.P. 715,074 (1933) and G.P. 612,266; *Chem.-Tech. Übersicht*, 1935, 59, 99.
65. F.P. 716,261 (1933).
66. U.S.P. 1,892,398 and 1,892,400 (1933).
67. U.S.P. 1,892,397; B., 1934, 55.
68. U.S.P. 1,890,772; B., 1934, 10.
69. *Ann.*, 1840, 35, 301.
70. The Miners Laboratories Bulletin, No. 2, 1925, p. 31.
71. D. H. Killefer, *Ind. Eng. Chem.*, 1926, 18, 1217.
72. A. Classen, F.P. 727,335; *Chem. Abs.*, 1932, 5105.
73. P. Below, *Mastoboino-Zhirovoe Delo*, 1931, 10, 22; *Chem. Abs.*, 1932, 4603.
74. U.S.P. 1,838,109 (1932).
75. F.P. 720,424 (1931).
76. O. A. Cherry and F. Kurath, U.S.P. 1,894,580; B., 1933, 929.
77. U.S.P. 1,665,234 and 1,665,233.
78. L. Meunier, F.P. 23,821 and 472,384 (1914).
79. *Kunststoffe*, 1922, 12, 164.
80. G. H. Malus and M. Phillips, *Chem. Met. Eng.*, 1921, 24, 661, and U.S.P. 1,441,598 (1923).
81. J. P. Trickey, C. S. Miner, and H. J. Brownlee, *Ind. Eng. Chem.*, 1923, 15, 65, and *Fr. Peters, ibid.*, 1936, 28, 756.
82. U.S.P. 1,873,599 (1932).
83. A. E. Williams, *Chem. Age*, 1933, 369, and Meunier, *Mat. grasses*, 1916, 9, 4516
84. *Annali Chim. Appl.*, 1936, 26, 3211; B., 1937, 61.
85. U.S.P. 2,095,250; B., 1940, 551.
86. *Sitzungsber. Preuss. Akad. Wiss., Berlin*, 1918, p. 201.
87. B.P. 234,862; B., 1925, 642.
88. U.S.P. 1,835,510; B., 1932, 902.
89. *Chem. Abs.*, 1931, 25, 5047.
90. U.S.P. 1,884,747; B., 1933, 721.
91. *Chem. Abs.*, 1932, 4493.

92. A. Peacock, B.P. 221,475 (1923); 219,368 (1923); and J. S. Stokes, B.P. 167,490.
 93. U.S.P. 1,857,357; B., 1933, 317.
 94. G. H. Mains, U.S.P. 1,841,138 (1932).
 95. U.S.P. 1,558,442 (1925).
 96. B.P. 359,047 (1930); U.S.P. 1,917,248; B., 1934, 414.
 97. *Res. Electrotechn. Lab., Tokyo*, 1926, No. 178.
 98. *Mod. Plastics*, 1936, 14, No. 2, 33; 1937, 15, No. 2, 24, 74; and 1938, 16, 32.
 99. *Ind. Eng. Chem.*, 1939, 31, 178.
 100. W. H. Moss, U.S.P. 1,902,256 (1933).
 101. *Chem. Abs.*, 1931, 25, 5047; *Chem. Zentr.*, 1932, 1, 296.
 102. Meunier, *Mat. grasses*, 1916, 4576; Mains and Phillips, *Chem. Met. Eng.*, 1921, 24, 681.
 103. U.S.P. 1,827,824; B., 1932, 737.
 104. Moss and White, U.S.P. 1,902,255 (1933).
 105. U.S.P. 1,825,307 and 1,894,580; B., 1933, 920.
 106. Montgomery and Ernest, *Chem. Met. Eng.*, 1921, 25, 335; British Thomson-Houston Ltd., B.P. 360,380 (1932).
 107. Cherry and Kurath, U.S.P. 1,890,069 (1933); B., 1933, 920.
 108. J. C. Patrick, U.S.P. 1,996,487; B., 1936, 464.
 108A. U.S.P. 2,114,877 (1938).
 109. Mead Corporation, B.P. 484,248; B., 1938, 1330.
 110. E. Rheinberger, B.P. 500,519; B., 1939, 631.
 111. G. J. Esselen and F. S. Baron, *Ind. Eng. Chem.*, 1938, 30, 125.
 112. G. S. Petrov, *Prom. Org. Chim.*, 1938, 5, 732; B., 1939, 172.
 113. R. A. van Linge, B.P. 506,533; B., 1939, 966.
 114. *J. Amer. Chem. Soc.*, 1938, 60, 1467.
 114A. I.G., B.P. 487,604; B., 1938, 1192.
 115. U.S.P. 2,146,655.
 116. U.S.P. 2,077,884.
 117. U.S.P. 2,168,169.
 118. *Chemical Age*, 1940, 43, 194.
 119. T. Aida, Jap.P. 113,672 (1936).
 120. *Ind. Eng. Chem.* (News Ed.), 1928, 4, No. 6.
 121. W. Nagel, *Z. angew. Chem.*, 1928, 41, 685.
 122. G. S. Petrov, *Plastics*, 1926, 2, 391, 436, 445.
 123. B.P. 223,636; B., 1925, 16.
 124. Dunlop Rubber Co. Ltd., B.P. 423,444; B., 1935, 321; B.P. 420,386; B., 1935, 111; Farbenfabrik vorm. F. Bayer & Co. G.P. 409,783; B., 1925, 461.
 125. F. Hassler, G.P. 407,713; B., 1925, 642.
 126. *India Rubber J.*, 1933, 86, 591; B., 1933, 1018; Ellis-Foster Co., Ltd., U.S.P. 1,927,929; B., 1934, 638.
 127. Ges. für Chem. Ind. in Basel, G.P. 401,168; B., 1925, 216; *Kolloud Beihefte*, 1933, 37, 343, 378, 385; B., 1933, 639; *ibid.*, 1934, 40, 1.
 128. *Brit. Plastics*, 1936, 8, 60.
 129. *Brit. Plastics*, 1938, 10, 896.
 130. *Ind. Eng. Chem.*, 1938, 30, 125; J. C. Patrick, *Trans. Faraday Soc.*, 1936, 32, 347; U.S.P. 1,890,191; B., 1933, 757; *Ind. Eng. Chem.*, 1936, 28, 1145.
 131. G.P. 569,021 (1933).
 132. I.G. Farbenind. A.-G., B.P. 489,437; B., 1939, 178.
 133. G. Walter and collaborators, *Kolloud-Beihefte*, 1933, 37, 343, 379, 385; B., 1933, 639.
 134. G. Walter, G.P. 569,021; *Chem. Abs.*, 1933, 27, 2321.
 135. British Celanese, Ltd., B.P. 416,949; B., 1934, 1070.
 136. G. Walter and collaborators, *Kolloud-Beihefte*, 1934, 40, 29; B., 1934, 1020.
 137. I. Allen, V. Meharg, and J. H. Schmidt, *Ind. Eng. Chem.*, 1934, 26, 663.
 138. U.S.P. 1,961,579; B., 1935, 368.
 139. *Bull. Soc. Chim.*, 1934, 990.
 140. U.S.P. 1,953,971.
 141. B.P. 506,999; B., 1939, 967.
 142. *Monatsh.*, 1890, 1, 199.
 143. *Ber.*, 1872, 5, 25.
 144. *Ber.*, 1881, 14, 350.
 145. Claisen and Ponder, *Ann.*, 1884, 223, 141.
 146. *Ber.*, 1901, 34, 1530; 1903, 36, 1575; 1909, 42, 1387.
 147. *J. Chem. Soc.*, 1904, 87, 20.
 148. *Ber.*, 1921, 54, 192.
 149. *Ind. Eng. Chem.*, 1928, 20, 599.
 150. *Report of the Chemistry Research Board*, 1934, p. 41.
 151. *Chem. Ind.*, 1938, 885.
 152. DuPont de Nemours & Co., U.S.P. 2,088,577.
 153. *Ber.*, 1934, 67, 1773.
 154. G. S. Whitby and J. R. Katz, *J. Amer. Chem. Soc.*, 1928, 50, 1160.
 155. S. L. Langedijk, *Chem. Ind.*, 1938, 891.
 156. Kluyver and Donker, *Kon. Acad. Wetensch.*, 1925, 35, 95.
 157. Carleton Ellis, *The Chemistry of Petroleum Derivatives*, 1934, 378.
 158. A. E. Maze, U.S.P. 1,683,835; B., 1929, 530.
 159. B.P. 411,483; B., 1934, 726.
 160. *Ind. Eng. Chem.*, 1933, 25, 997, and J. C. Kanow, U.S.P., 2,213,549.
 161. *Brit. Plastics*, 1938, 10, 607.
 162. *Bad. A.S.F.*, G.P. 837,933.
 163. *Ibid.*, B.P. 170,351 (1929).
 174. H. Dreyfus, B.P. 181,575 (1921).
 165. *Bad. A.S.F.*, G.P. 839,107.
 166. G.P. 420, 414.

167. U.S.P. 1,537,221; B., 1926, 68.
168. *Chem. Zentr.*, 1925, 1723; *Swiss P.* 149,420; *Kunst.*, 1933, 23, 117.
169. G. Steinmeg, U.S.P. 1,883,060; *Chem. Abs.*, 1933, 27, 857; Frinkelstein, U.S.P. 1,900,700; *Chem. Abs.*, 1933, 27, 3093.
170. Bad. A.S.F., G.P. 407,668 (1922).
171. I.G. Farbenind., A.-G., U.S.P. 1,933,986; *Chem. Abs.*, 1934, 28, 664; A. V. Blom, *Kolloid-Ztg.*, 1933, 65, 223.
172. Bad. A.S.F., G.P. 412,913 (1923).
173. J. Y. Johnson, B.P. 407,997; B., 1934, 591.
174. *Ber.*, 1874, 7, 1605.
175. *J. Amer. Chem. Soc.*, 1902, 24, 752.
176. G.P. 207,743 (1907).
177. Vingtrie, F.P. 493,569 (1916); Bayer & Co., G.P. 349,741 (1918); Folchi, *Chem.-Ztg.*, 1922, 46, 714.
178. G.P. 403,264; B., 1925, 216.
179. N. J. L. Megson and Pepper, *Chem. Ind.*, 1940, 252.
180. G.P. 406,999; B., 1925, 461.
181. S. K. Smith, H. Dodd, and I.C.I., B.P. 488,110; B., 1939, 176.
182. B.P. 314,810; 497,413; *Chem. Abs.*, 1930, 24, 3663.
183. DuPont de Nemours & Co., U.S.P. 1,982,676.
184. *J. Chem. Soc.*, 1932, 2251.
185. R. S. Morrell, S. Marks, and H. Samuels, *J.S.C.I.*, 1933, 52, 130 T; B.P. 407,957; B., 1934, 511.
186. N. K. Adam, Morrell, and Samuels, *ibid.*, 1934, 53, 255 T; A. H. Hughes, *J.C.S.*, 1933, 338.
187. B. T. Brooks and E. J. Cardarelli, U.S.P. 1,860,730 (1932), and O. Diels, *Z. angew. Chem.*, 1929, 42, 911.
188. Carleton Ellis, *Ind. Eng. Chem.*, 1936, 28, 1130; E. R. Littmann, *ibid.*, 1150; A. V. Blom, *Chemie u. Technologie der Kunststoffe*, 1939; Hercules Powder Co., G.P. 653,420.
189. U.S.P. 2,047,004; B., 1937, 1374.
190. B.P. 492,934; B., 1939, 295; Oelwerke Noury and van der Lande, B.P. 530,916 (1941).
191. *Ber.*, 1930, 63 (13), 3213; A., 1931, 198.
192. I.G. Farbenind., A.-G., G.P. 540,101 (1930); Kranzlein, Voss, and Dickhauser, G.P. 547,384 (1930).
193. Carleton Ellis, *Ind. Eng. Chem.*, 1933, 25, 126.
194. R. S. Morrell and W. R. Davis, *J.S.C.I.*, 1936, 55, 101 T.
195. S. L. Malowan, *Farbe u. Lack*, 1934, 39, 30; *Rev. Gén. Mat. Plast*, 1934, 10, 346.
196. I.G. Farbenind., A.-G., B.P. 346,550; 352,042; 353,926; B., 1931, 666, 853, 1132; *Amer. Chem. Abs.*, 1935, 29, 2261.
197. J. B. Rust, U.S.P. 2,069,725; B., 1939, 636.
198. Harvel Corporation, U.S.P. 2,051,765-68; B., 1938, 1077.
199. Howroyd, McArthur & Co., G.P. 638,218.
200. *Brit. Plastics*, 1935, 6, 503; B., 1935, 562.
201. Industrial Sugar Products Corp., U.S.P. 1,949,831-2; B., 1935, 70.
202. *ibid.*, 1,974,064; B., 1935, 737.
203. Weiss and Downs, Inc., U.S.P. 1,999,380; *Chem. Abs.*, 1935, 29, 4102.
204. N. D. Scott and J. F. Walker, *Ind. Eng. Chem.*, 1940, 32, 312.
205. G.P. 632,299.
206. *Chemical Age*, 1940, 303.
207. I.C.I., B.P. 520,022 and 521,545 (1940); DuPont de Nemours & Co., Ltd., B.P. 518,657.
208. H. Barron, *Chemical Age*, 1941, 108, and L. Light, *ibid.*, 1941, 26.
209. I.G., B.P. 523,130.
210. I.G., U.S.P. 2,187,817.
211. B.P. 487,355; B., 1939, 177.
212. *Brit. Plastics*, 1938, 10, 36.
213. B.P. 531,535.

CHAPTER XIV

ELECTRIC TESTING AND REQUIREMENTS

By R. P. L. BRITTON

IN the past the selection of good insulating materials has been largely made by the mechanical suitability of the substances, and the effectiveness of the insulation has been secured by the design and the factor of safety incorporated. Recently, however, the situation has undergone a change; the British Electrical and Allied Industries Manufacturers Association and the Electrical Research Association connected with it, together with the British Standards Institution, are drawing up Standard Specifications and methods of testing. Similar conditions hold abroad, e.g. the Bureau of Standards and the A.S.T.M. (American Society of Testing Materials) in the U.S.A. The Verband Deutscher Elektrotechnik in Germany are also correlating the various results and exploring avenues of research for the future. It will in the nature of things be some time before this work will make its full force felt, but the ultimate effect on the industry must be great, resulting in saving of space, compactness of design, increased efficiency of machines, and possibilities of manufacture hitherto undreamt of. The insulators of the future will alter the design of electric machinery, and make to appear clumsy what now seems compact.

In an 'ideal' insulator, if such existed, when an alternating voltage is applied, a charging current will flow exactly a $\frac{1}{4}$ cycle out of phase, or 'in quadrature' with the voltage, the one being a maximum when the other is zero. No ideal insulator exists, and in practice a combination of the conditions for conductors and the conditions for insulators exists together. In a really good insulator the very small current which passes is nearly all 'in quadrature' with the voltage, but a minute part of it is made up of 'leakage' current 'in phase' with the voltage. The 'in quadrature' current causes no energy loss, but the 'in-phase' current, in conjunction with the voltage applied, represents an energy loss which is shown up as heat produced. In



FIG. A



FIG. B

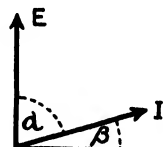


FIG. C

all direct current work, and even in alternating work, where the voltage and current are in phase with one another, the power

expended in the circuit is expressed as the product of the current (amps) and the pressure (volts), the unit of energy being the *watt*. But when the two are 'out of phase', even by a small amount, then the power expended is less than the apparent power. Thus:

$$\text{True power} = \{\text{Apparent power (i.e. volts} \times \text{amps.)}\} \times \{\text{Factor}\},$$

the factor being 1 or very nearly 1 when the current and volts are in phase or nearly in phase.

In the case of an insulator, the current and voltage are very nearly completely 'in quadrature', and the factor is therefore very nearly zero. This factor is known as the *power factor*, cf. Chapter III, p. 164. If a more mathematical conception of the meaning of power factor is necessary, a 'vector' diagram will serve best. In Fig. A are shown voltage and current 'in phase' and the power factor is unity. In Fig. B the voltage and current are 'in quadrature', and the power factor is zero.

In Fig. C we see represented the conditions which apply to *insulators* in practice. The current is not quite 'in quadrature' with the voltage, the 'in-phase' angle, or *phase angle*, being α , and the 'off-quadrature' angle, or *loss angle*, being β . The phase angle and the loss angle are complements of one another, and when β is small, as in the case of good insulators, the power factor is almost equal to the loss angle itself expressed in radians, or to the cosine of the phase angle. The phase angle is most usually referred to in electrical work as the Greek letter ϕ , and hence the expression $EI \cos \phi$ appears frequently as a definition of the true power being expended in an alternating current circuit.

All dielectrics are seriously affected by heat, both insulation resistance and dielectric strength being diminished. If the composition be such that this is unaffected by the temperature, these reduced values are permanent as long as the temperature is maintained, but rise again as the temperature falls (cf. pp. 168, 171). If, on the other hand, the composition be unstable under heat, these values will fall and go on falling, if decomposition continues. If, however, the change were to be only partial and then reach a stable state, both insulation resistance and dielectric strength would fall initially, reach a minimum, and then rise until stable values were obtained at a steady temperature. These values may be higher or lower than the initial values in the cold condition, but on cooling they would rise much higher than they were at the elevated temperature. This latter condition applies to all imperfectly cured insulators and also to those insulators which have absorbed water or other liquids.

If the insulation resistance of a dielectric be low, electricity will pass through it and the passage of this current will cause heat which will result in a rise of temperature. If the insulator be of the type which is unstable but reaches stability and the application of the potential be gentle, the current will gradually cause a stable condition to occur. With all organic insulators, however, of whatever type,

there will be a temperature at which instability will take place. In consequence, if the potential be increased in steps, or the temperature be similarly increased, allowing conditions to attain equilibrium at each step, a point will be reached at which equilibrium is no longer possible and the material becomes unstable and breakdown occurs.²⁰ The voltage just below this is the 'highest maintained electric stress'.¹ Repeated applications of voltages below this will leave the insulator unchanged. The application of voltages above this value for short periods may not cause the dielectric to break down, but will permanently strain it and alter its characteristics.

The strength of the dielectric or its breakdown voltage is of prime importance; this will be less at high temperatures than at low ones. In practice stresses are limited by considerations of thermal balance more than by the ultimate strength of material stressed.⁷ If the test is applied suddenly with rapidly increasing pressure, a comparatively high value for the *Breakdown Voltage* or dielectric strength will be obtained. This is called the *Instantaneous Value*.

If some *arbitrary* time for applying the stress be taken, as, for instance, 1 minute, another value will be obtained. This is called the *Minute Value*. If the voltage be applied in successive stages, allowing each to attain equilibrium, a still smaller value will be obtained and the voltage at the last stable stage is called the *Highest Maintained Electric Stress*. According to Whitehead,¹ the most important feature of breakdown is the development of a high unstable conductivity connoting the loss of insulating properties. The insulation resistance is of importance, because if it be low decreased efficiency will result. The effect of low insulation is cumulative, as leakage causes a rise in temperature and this in turn causes more leakage, so that unless equilibrium is reached breakdown would inevitably occur. The surface of the insulation might become coated with moisture or affected in nature by chemical influences, light, &c., and in consequence possess a different electrical resistance from the mass or volume. It sometimes happens that the surface is so affected as to become conducting, although the main mass is still a good insulator. In consequence it becomes necessary to measure both the surface resistance and the volume resistance. Until quite recently the breakdown voltage (B.D.V.) and insulation resistance were the two electrical criteria of insulating materials, the other deciding factors being of a mechanical and chemical nature. The Electrical Research Association have standardized the methods of test and also for power purposes have suggested the determination of the highest maintained electric stress, and for radio purposes the determination of the *Loss Angle* or of the *Power Loss*. According to Dellinger and Preston,⁷ the simplest constant involved in expressing this loss is loss angle. If this be taken in radians it equals the power factor (provided this figure is small, which is true for nearly all insulating materials suitable for use in measuring apparatus). If the loss angle be taken in degrees, then it requires to be multiplied by 1.75 in order to equal the power factor in percentage. These

tests are very searching and show up in a new light what have been in the past regarded as good insulating materials.

A typical purchasing specification as issued by the British Standards Institution includes mechanical and chemical tests, resistance to moisture (tested electrically), the effects of acids or oils where necessary, and a durability or ageing test. The dielectric strength test is usually taken at 90° for varnish; viscosity test, flash-point, specific gravity, colour, and acidity are included (see B.S.S. 119, Clear Baking Oil Varnish). For solids insulation resistance tests are given for both volume and surface insulation, and if laminated, mechanical and electrical strength tests along the laminae are included (see B.S.S. 316). For machines (see B.S. Specification No. 168) a table of high voltage tests is given. The insulation resistance shall be measured in megohms, and when the high voltage test is applied shall not be less than

$$\frac{\text{rated volts}}{1,000 + \text{rated output in kVA. or B.H.P.}}$$

The American Institute of Electrical Engineers recommend that the insulation resistance of the complete apparatus should be such that it does not send more than one-millionth of the rated load current at the rated terminal voltage through the insulation. Where the value in this way exceeds 1 megohm it shall be considered usually sufficient. Definite figures for insulation must be regarded with very great caution.

It will be obvious from the foregoing that the method of test will have a very great bearing upon the value obtained, and also that varnishes compounded from resins and oils have a very different value from the ingredients themselves.

The dielectric strength is a prime factor, and a few values are given for comparison.

Phenol-formaldehyde resin	.	.	.	200-500 v./mil
Shellac	.	.	.	450-600 v./mil
Congo, Sandarac	}	.	.	350-450 v./mil
Manila, Pontianak		.	.	
Boiled linseed oil	.	.	.	370 v./mil
Cellulose acetate	.	.	.	400-700 v./mil
Furfural-cresol resin	.	.	.	170 v./mil
Acrolite (Glycerine-phenol)	.	.	.	720 v./mil
Transformer oil	.	.	.	500 v./mil
Bitumens	.	.	.	250-1,000 v./mil
Rubber	.	.	.	700-750 v./mil

Wire Coverings

Asbestos	50 v./mil
Cotton	140 v./mil
Silk	450 v./mil
Enamel	1,000 v./mil

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W. S. Flight⁸ gives the following values per $\frac{1}{16}$ in. thickness.

Material	B.D.V. in air		Change
	at 30° C.	at 100° C.	
Paper (untreated)	12 kv.	13.7 kv.	Per cent. +14.0
Micarta	27.9	7.7	-75.0
Fuller board	18.0	16.8	-6.7
Varnished cloth	27.8	16.2	-41.6
Varnished paper	24.8	17.2	-30.6
Varnished asbestos paper	7.3 H	1.2 H	-84
Fibre	7.5 H	1.5 H	-80.0

H = humidified.

Similar tests taken with the insulators immersed in transformer oil.

Material $\frac{1}{16}$ in.	B.D.V.		Change
	at 30° C.	at 100° C.	
Paper (untreated)	32.2 kv.	23.5 kv.	Per cent. -27.0
Micarta	28.8	11.8	-61.0
Fuller board	27.0	17.5	-35.0
Varnished cloth	30.7	23.1	-24.6
Varnished paper	38.5	17.7	-54.0
Varnished asbestos paper (dried)	15.0	8.4	-44.0
Fibre	25.0	7.5	-70.0

Harvey L. Curtis⁹ gives the following values for surface resistance and volume resistance taken in air at 90-100 per cent. humidity.

	Surface resistance	Volume resistance
Ceresin	$10^{16} \Omega/\text{cm.}^2$	$5 \times 10^{17} \Omega/\text{cm.}^3$
Special paraffin	$10^{16} \Omega/\text{cm.}^2$	$10^{17} \Omega/\text{cm.}^3$
Paraffin	$7 \times 10^{14} \Omega/\text{cm.}^2$	$10^{15} \Omega/\text{cm.}^3$
Bakelite No. 558	$9 \times 10^{13} \Omega/\text{cm.}^2$	$2 \times 10^{14} \Omega/\text{cm.}^3$
Yellow beeswax	$5 \times 10^{13} \Omega/\text{cm.}^2$	$3 \times 10^{14} \Omega/\text{cm.}^3$
Resin	$2 \times 10^{13} \Omega/\text{cm.}^2$	$5 \times 10^{15} \Omega/\text{cm.}^3$
Sulphur	$10^{13} \Omega/\text{cm.}^2$	$5 \times 10^{16} \Omega/\text{cm.}^3$
Sealing wax	$8 \times 10^{13} \Omega/\text{cm.}^2$	$8 \times 10^{14} \Omega/\text{cm.}^3$
Amber	$6 \times 10^{11} \Omega/\text{cm.}^2$	$5 \times 10^{15} \Omega/\text{cm.}^3$
Shellac	$10^9 \Omega/\text{cm.}^2$	$10^{15} \Omega/\text{cm.}^3$
Micanite	$3 \times 10^8 \Omega/\text{cm.}^2$	$10^{14} \Omega/\text{cm.}^3$
White mica 5	$5 \times 10^8 \Omega/\text{cm.}^2$	$2 \times 10^{16} \Omega/\text{cm.}^3$
Celluloid	$10^8 \Omega/\text{cm.}^2$	$3 \times 10^9 \Omega/\text{cm.}^3$
Glass (cavalier)	$10^8 \Omega/\text{cm.}^2$	$8 \times 10^{14} \Omega/\text{cm.}^3$
Hard rubber	$10^8 \Omega/\text{cm.}^2$	$10^{17} \Omega/\text{cm.}^3$
Red fibre	$2 \times 10^7 \Omega/\text{cm.}^2$	$5 \times 10^8 \Omega/\text{cm.}^3$
Fused quartz	$2 \times 10^7 \Omega/\text{cm.}^2$	$5 \times 10^{17} \Omega/\text{cm.}^3$
Unglazed porcelain	$6 \times 10^6 \Omega/\text{cm.}^2$	$5 \times 10^{15} \Omega/\text{cm.}^3$
Ivory	$4 \times 10^6 \Omega/\text{cm.}^2$	$2 \times 10^{17} \Omega/\text{cm.}^3$
Red marble (Tennessee)	$3 \times 10^6 \Omega/\text{cm.}^2$	$5 \times 10^8 \Omega/\text{cm.}^3$
Plate glass	$2 \times 10^6 \Omega/\text{cm.}^2$	$2 \times 10^{13} \Omega/\text{cm.}^3$
Italian marble	$2 \times 10^6 \Omega/\text{cm.}^2$	$10^9 \Omega/\text{cm.}^3$
Blue marble	$10^6 \Omega/\text{cm.}^2$	$10^6 \Omega/\text{cm.}^3$
Slate	$10^6 \Omega/\text{cm.}^2$	$10^7 \Omega/\text{cm.}^3$

*Specific Inductive Capacities (Dielectric Constants)*⁵¹

Amber	2.86	Mica (silver)	5.0
Asphalt	3.0	Paper	2-2.8
Bakelite	4-6	Paraffin wax	2-2.3
Celluloid	4-16	Pitch	1.8
Ebonite	2-3.5	Resin	3.5
Glass (common)	3-3.25	Shellac	2.75
Glass (flint)	6-7	Silk (density 1.51)	4.6
Gutta-percha	3.1	Sulphur	3-4
Indiarubber (pure)	2.12	Yellow varnished cloth	5.5
Indiarubber (hard)	3.0	Black varnished cloth	4.5
Mica (muscovite)	7.0		

The specific inductive capacity (dielectric constant) is a factor that by itself is only of theoretical interest. Its bearing on the quality of the insulation is somewhat complex, and in consequence a word of explanation will not be out of place. According to Whitehead,¹¹ a previously uniform electric field will be distributed among insulators of varying S.I.C.s introduced therein in such a manner that the first insulator to break down will be the one having the lowest product of its S.I.C. and B.D.V. (for respective thickness). At first sight this would seem to indicate that it is advisable to have an insulator with a high S.I.C. This conclusion, however, is unjustifiable, as whilst it is true that in a piece of apparatus employing composite insulators less electric stress will be exerted on the material of high S.I.C., it is just as disadvantageous to have a breakdown in one insulator as in another, the strength of the chain being the strength of the weakest link. Furthermore, if the apparatus be designed to work in air, a large field will be imposed upon the surrounding air (air being an insulator), and unless the air-layer between points of different potential be large enough, either corona or breakdown will occur. This corona would exert a serious effect upon the surface of the insulation and surface leakage would take place. It can be seen that the essential feature in a piece of apparatus is to have, as far as possible, a uniform S.I.C. throughout, or to have the material with the highest S.I.C. situated in the centre of the field and the other materials of lower S.I.C.s grading outwards, so that the product of their S.I.C. and B.D.V. shall all be equal. These conditions apply more or less in 'oil-cooled transformers' and explain why high voltage tests for 'breakdown' are frequently conducted under castor oil, &c. in order to prevent corona or spark-over.

Insulators, however, are never judged on S.I.C., although the related power loss is an important feature. The variation of S.I.C. with temperature in the majority of cases is not very large, provided the materials are perfectly dry. The presence of moisture, however, results in large variations. The S.I.C. increases fairly rapidly with increase of frequency, but, according to L. Hartshorn,¹² there is no discrepancy between the values obtained with direct and alternating currents, provided that the direct current observations are made after times of charge or electrification of the same order as the periodic times of the alternating current. The conclusion that he comes to is

that 'the power dissipated under such circumstances, in the frequency range of 50-800 cycles may be entirely accounted for by the phenomena of dielectric absorption and normal conduction.

No attempt to classify insulators according to their chemical composition has so far been satisfactory. The most one can say is that increasing molecular complexity results in improved electrical insulating qualities. It is possible that future advance will be made along these general lines. According to Güntherschulze:¹³

'As far as elements are concerned, increasing complexity results in decreasing insulating qualities, atoms of higher atomic number than 16 tending to become conductors. True dielectrics are homogeneous substances which insulate, because their atoms are able to retain their valency electrons, owing firstly to the great difference between the distance of the electrons from their own nucleus and from external nuclei, and secondly to the small shielding effect of the electrons in the inner ring or rings. The larger the atom the greater the shielding effect of the inner electrons, so that as far as elements are concerned, only those of low atomic number, having the external ring nearly complete, form good dielectrics. We see, therefore, that true dielectrics such as hydrocarbons, resin, rubber, and so on, consist essentially of Hydrogen (atomic no. 1), Carbon (atomic no. 6), Oxygen (atomic no. 8), Sulphur (atomic no. 16). Elements of higher atomic number rarely, if at all, exist as true dielectrics.'

He classifies insulating materials as true and pseudo-dielectrics, the latter term being used to describe non-metallic substances which contain ions capable of migration in an electric field. Such passages are of course opposed by viscosity, and in view of the high internal friction at normal temperatures of most solid materials, their insulation is high. When, however, the temperature is raised, the internal friction decreases and a rapid decrease of insulation results. He classifies glass and porcelain as pseudo-dielectrics and points out that true dielectrics become pseudo-dielectrics if they contain ionic impurities.

According to E. B. Wedmore,¹⁴ the breakdown strength of a liquid depends, in many cases, more upon the nature of the impurities than upon the nature of the liquid.

The Electrical Research Association have shown that 20-30 milligrams of cotton fibre per 10,000 c.c. of oil resulted in a reduction of breakdown strength of 30 per cent., but if moisture were also present the reduction was 90 per cent., according to E. B. Wedmore.¹⁴ When a difference of potential is applied to a pair of electrodes immersed in a liquid a small conduction current at first passes. If the voltage be raised sufficiently, an unstable rise in the current takes place at certain potentials, which may discharge the circuit or may result in the formation of an arc if the available power be adequate. In practice this sudden rise of current generally opens the circuit automatically.

This instability of current is accompanied by a flash, with some amount of decomposition of the liquid and the production of gas; this is termed spark-over.

The same remarks apply to the breakdown of solids.

According to Schumann,¹⁵ two types of breakdown in solids may be considered:

- (1) Physical breakdown with small mechanical damage, as with crystalline substances and siliceous materials.
- (2) Industrial breakdown where thermal instability and extensive damage occurs.

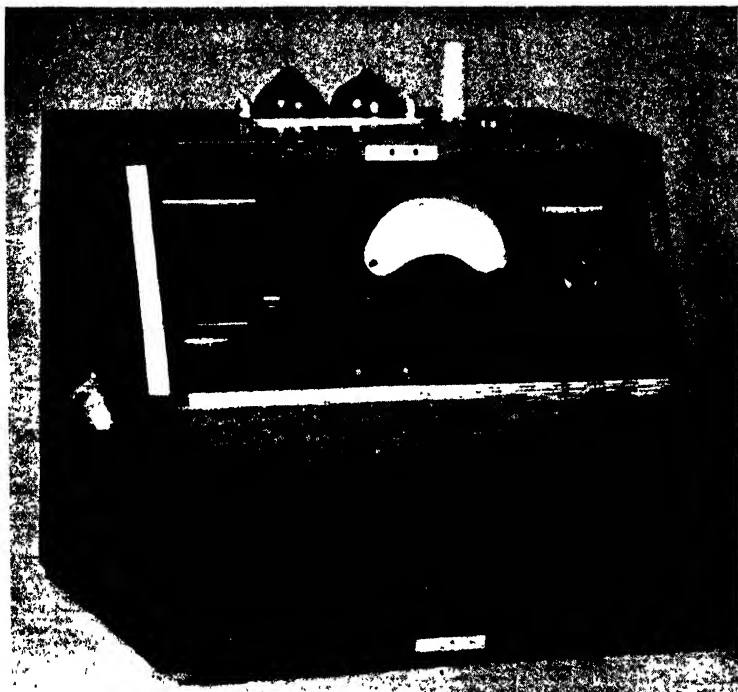


FIG. 38. Testing Transformer, by Ferranti, for testing the breakdown of insulating materials. Suitable for voltages up to 20,000 volts

This thermal instability has been dealt with earlier in this chapter.

The Director of Research,⁶ E.R.A. (Electrical Research Association), in a discussion on the theory of thermal instability, shows that there are critical voltages and temperatures for all insulators, and that if temperature be suppressed, voltage may go on rising without reaching a critical stage; thus breakdown is dependent on heat dissipation. This heat dissipation may be due to inherent qualities of the insulator or to artificial cooling conditions. Given, however, a stable ambient temperature, the heat dissipation is purely a function of the insulator itself. Thus we see that in order to approach an ideal insulator we have to obtain great complexity, freedom from

ionic impurities, and ready dissipation of heat. It is difficult to reconcile these opposing factors, but some move in this direction may be made by increasing the internal viscosity and getting rid of ionic impurities. There is another feature of molecular composition which has to be borne in mind: increasing complexity is most easily obtained by the presence of polar groups in the molecule. Now it is known that these groupings tend to give anomalous results in electrical insulation.^{1,3,15}

Accordingly, so far as we are able to discuss chemical structure as related to insulating qualities, we may summarize our knowledge in the following hypothesis.

Polar groupings give complexity, and complexity gives insulation. When, however, a complex body is obtained free from polar groupings such a body is an insulator and more closely approximates to straight-line laws.

L. Hartshorn and E. Rushton,¹⁰ dealing with the 'Dielectric behaviour of some Thermoplastics', commented on the nature and uses of plastics of both the thermo-setting and thermoplastic types, and the manner in which widely variant and sometimes curious combinations of properties could be obtained by 'tailoring the molecule' (Carleton Ellis). They then dealt simply but effectively with the gradation of dielectric properties in a series of resins prepared from phenol, cresol, xylenol, and benzyl alcohol, with formaldehyde. Applying Debye's Theory³ to observations of power factor, it is possible to calculate the relative radius of rotation of the molecule in the substance under test, and the values obtained in Hartshorn's experiments were substantially equal to the radius of the (OH) group as determined by X-rays: this suggests that the motion of the polar (OH) groups of the resins under the alternating field is responsible for 'Power Factor'. Since the comparatively high power factor of the phenolic resins can be attributed to polar (OH) groups, their replacement by hydrogen giving a hydrocarbon structure should give superior insulation. In ordinary phenolics the absorption of water under ordinary conditions is up to 3-5 per cent., whereby the power factor is raised by 50 per cent. Polystyrene and polyindene containing no polar groups give very low power factors (styrene as low as 0.0002) and a low dielectric constant (about 2.5).

Debye's Theory³ referred to above states: 'If the molar polarization (in an electric field) depends on temperature, the molecule is polar. If it does not it is non-polar.' This 'temperature' refers, of course, to only small changes and not to the instability values discussed under 'Highest Maintained Electric Stress'. The 'composition' discussed is the 'true chemical composition', and not the 'compounding' or 'technical composition' which may contain solvent, or moisture, &c., and which has been dealt with on pp. 382, 383.

For general considerations of electric tests the reader is referred to *A Critical Resumé of Recent Work on Dielectrics*, B.E.A.I.R.A. report L/T 14.²¹ More recent work is summed up in the words of Whitehead:

'The inherent properties of solid insulating materials will, irrespective of other improvements, ultimately limit their exposure to very high voltages and field strengths. In circumstances where more or less uniform thermal and electric fields cannot altogether be avoided, thermal instability sets a limit to the voltage which may be dealt with in a single unit. At lower voltages and under more favourable thermal conditions, ionization may form an important limitation to the field strengths which may be used, although the quantitative application of such principles is not yet possible. Apart from this, however, the field strength is limited by the "Intrinsic" electric strength which appears associated with the ultimate structure of the material.'

These three properties, 'Thermal Instability', 'Ionization', and 'Intrinsic Electric Strength,' have been the subject of recent research work by the Electric Research Association.

Whitehead,¹¹ dealing with 'Thermal Instability', says:

(i) 'Provided that a sufficiently wide range of thermal conditions is available, a dielectric will exhibit at least two types of breakdown, a Thermal and a Non-thermal type. In the case of Thermal Breakdown the electric strength corresponding to a long time of stress can be calculated with adequate accuracy from the conductivity under stable conditions when the external thermal conditions and also the thermal properties of the dielectric are known. Provided the electric strength so computed is less than the non-thermal electric strength the calculation will be valid whether breakdown takes the form of a progressive loss of insulating properties or the form of a sudden explosive discharge.

(ii) 'If a stronger field is applied so that breakdown takes place in a short time the theory of Thermal Instability may be extended to give the electric stress corresponding to this time of application. The quantitative agreement between theory and experiment is not then so accurate, but if the variation of electric strength with time is known for a given temperature, the variation at other temperatures can be deduced with sufficient accuracy.

(iii) 'A transition temperature exists for any given time of application of electric stress and given external conditions. Below this temperature non-thermal breakdown occurs, above it the electric strength obeys the theory of thermal instability. The range of application of the latter theory is accordingly confined largely to higher temperatures, thicker specimens, poorer dielectrics, longer times of application, or electrode arrangements of higher thermal resistance.'

Thermal instability is bound up with thermal conductivity. A material has 'unit conductivity' when it conducts 1 gram calorie of heat per second across opposite sides of a centimetre cube, the difference in temperature of the sides being 1° C.¹⁹ In considering heat transference in electrical machinery and apparatus, it is more convenient to express the above-mentioned property in terms of thermal resistivity. In its report on the heating of buried cables the B.E.A.I.R.A.²⁰ used the symbol $K^\circ \text{C.}$ to express thermal resistivity and defined it as the temperature difference in ° C. to cause a transfer of energy at the rate of 1 watt between opposite faces of 1 centimetre

cube. Some values found for different materials are given in the table below :

Pressboard	K° C.	= 400-600
Varnished board (2 sources)	K	= 320-97
Untreated Jap silk	K	= 2,050
Varnished „ „ 9 per cent. silk	K	= 627-778
Cotton cambric (5 mil)	K	= 600-800
„ „ varnished (7 mil)	K	= 100-270
Micanite	K	= 580-617
Mica silk	K	= 927-1,860
Mica cloth	K	= 768-1,460

Before technical application of 'Ionization' and 'Intrinsic Electric Strength' can be made, more fundamental work on these properties is required.

Fröhlich's theory is applicable only to non-polar crystals. It states that : 'Beyond a certain field strength, an electron may gain energy from the field and eventually ionize the lattice.' B. E. A. I. R. A.²¹ technical report shows methods by which 'Intrinsic Electric Strength' of solid dielectrics may be defined and evaluated. It is shown that the magnitude of the effect of temperature and thickness upon the electric strength of certain crystals agree with Fröhlich's theory, as also does the effect of disordered structure and micro-structure in certain instances. Mica obeys the theory very well over wide ranges of temperature. Complex organic substances do not obey the theory, and more work is necessary before definite conclusions can be drawn. Departure from the theory also occurs with crystals when certain limits of temperature are exceeded.

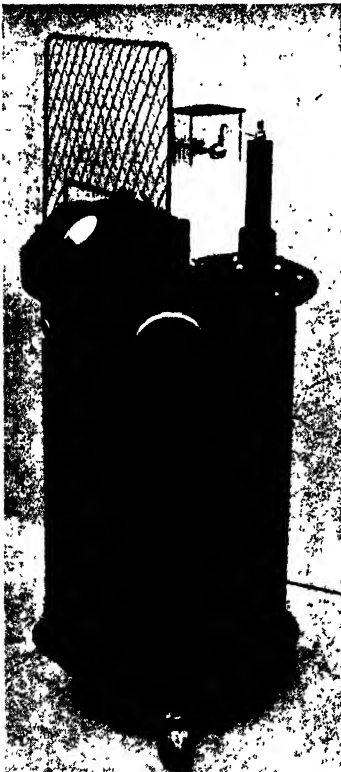


FIG. 39. Testing Transformer, by Ferranti, for testing the breakdown of insulators, solid compounds, &c., suitable for voltages from 20,000 to 50,000 volts

In the accompanying illustrations instruments for testing the electrical properties of insulators are shown.

Figs. 38 and 39 show Testing Transformers for taking the breakdown strength of dielectrics. No. 38 type is suitable for voltages up to 20 kilovolts. No. 39 type, supplied by Messrs. Ferranti, is suitable for voltages from 20 to 50 kilovolts.

Fig. 40 illustrates the Testing Electrode devised by the E.R.A., the test specimen being inserted between the copper blocks and these then connected up with the Testing Transformer. Figs. 41 and 42 show Low Tension Schering Bridges which provide a method of

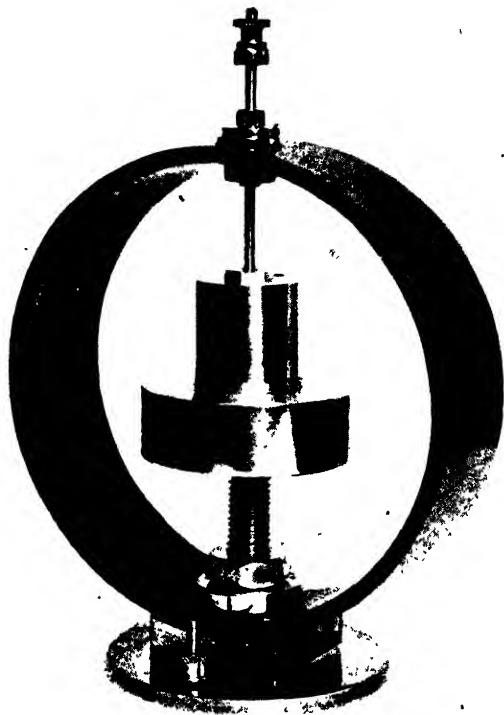


FIG. 40. Testing Electrode devised by the Electrical Research Association of the British and Allied Industries Manufacturers Association for testing varnishes

measuring the dielectric constant and the power factor of insulating materials. Two patterns are made: the Cambridge pattern, illustrated in Fig. 41, and the E.R.A. pattern, shown in Fig. 42, by the British Engineering Standards Institution, in their revised B.S.S. 234-1925, for the determination of the power factor of ebonite samples. The most suitable pattern for any particular purpose depends upon the thickness of the material to be tested, and also on whether commercial or precision methods are to be employed. In each bridge, the material forms the dielectric of a test condenser,

and the electrodes and leads are so screened that samples may be readily tested at a controlled temperature and humidity.

With the Cambridge pattern, measurements may be obtained of power factors from 0.001 to 0.5 with test capacitances varying from 100 to 1,000 micro-microfarads; the bridge is direct reading and easy



FIG. 41. Cambridge Pattern Low Tension Schering Bridge

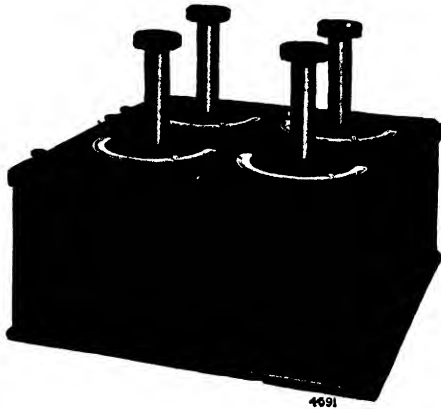


FIG. 42. E.R.A. Pattern Low Tension Schering Bridge

to operate. The test condenser normally supplied is suitable for samples not less than 150 mm. in diameter of high-quality insulating materials up to 1.6 mm. thick, and will test lower quality insulators up to 6.4 mm. thick. Other sizes of test condenser can be supplied for samples up to 9.5 mm. thick. The bridge network consists of the test condenser (which in this instance is actually one arm of the network), a calibrated variable condenser, and two equal high-resistance ratio arms shunted by variable condensers. One of these shunting condensers is uncalibrated, being used merely for balancing;

the other is calibrated directly in power factor at 800 cycles per second. The detector is a high resistance telephone, and the source is an 800 cycle fixed frequency oscillator. The form of electrodes depends upon the application for which the bridge is desired, e.g., solid dielectrics. Both patterns have been adapted for fabrics or

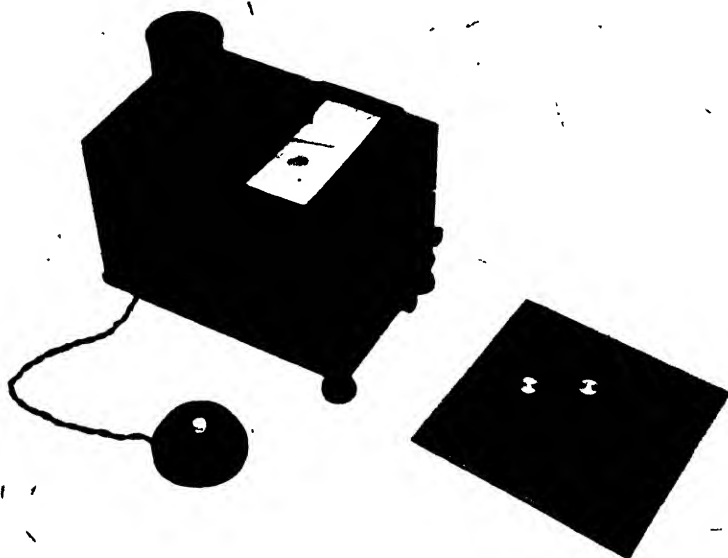


FIG. 43. Method of testing Surface Insulation Resistance, using a Megger by Evershed and Vignoles

insulating oils. The electrodes shown on the left of Fig. 41 are used when testing solid dielectrics. In using the bridge, readings are first taken without the dielectric between the electrodes (distance pieces, cut from the sample, are used to support the guard ring), then the samples are inserted, and a direct comparison obtained. Since a perfect air condenser is used in the initial test, complicated factors are eliminated, physical measurements of the thickness of the sample are unnecessary, and the method has the further advantage of being direct reading.

The bridge shown in Fig. 42 has been made to the specification of the British Electrical and Allied Research Association, for measurements of thin dielectrics such as paper, presspahn, thin mica, oil-silk, &c. Power factors of the order of 0.00045 have been determined with this pattern. It is, however, necessary to measure the dimensions of the sample very accurately.

The bridge network is similar to the Cambridge arrangement, but

Property	Paper base	Fabric base
Water absorption (B.S.S. 547) $\frac{1}{16}$ " thick . . .	0.15-2.5	1.5-2.5
Safe limit for constant temperature . . .	90° C.	90° C.
Electric strength (volts/mil) $\frac{1}{8}$ " thick at 90° C.	100-500	30-80
Dielectric constant	4.5-8	7-11
Volume resistivity (ohms/cm. ³)	10 ⁸ -10 ¹⁴	10 ⁸ -10 ¹⁰

Some work on the electrical behaviour with varying chemical composition has been undertaken by the B.E.A.I.R.A. L/T 89. They find that in a series Phenol → *meta*-cresol → *m*-5-xylene, the synthetic resins show practically the same dielectric strengths and values for permittivity and absorb practically the same quantity of water from the atmosphere. There is, however, a definite decrease in power factor in the series, 0.012 → 0.0087 → 0.005, which is ascribed to the addition of methyl groups to the structure.

The phenol-formaldehyde resins are liable to 'tracking' or 'treeing', i.e. the formation of conducting paths under surface discharge. This can be overcome by the use of surface varnishes.

The Thermoplastic or Novolak Type.

Some interesting work has been done by the B.E.A.I.R.A., ref. L/T 92. They find that at room temperatures the permittivity and power factor of the thermoplastic resins are about the same as those of the heat-hardened resin in the dried condition. At higher temperatures, however, the properties are different. In the region 60-100° the power factor (at audio-frequency) rises from a value of about 0.005 to a fairly sharp maximum of 0.1 or more. The peak in the power factor curve is accompanied by an increase in permittivity with rise of temperature, and undoubtedly indicates some physical process (such as the orientation of polar molecules). Further work (L/T 94) leads to the conclusion that observed absorption and dispersion effects in both resins are due to the orientation in the electric field of the (OH) groups which form part of the molecule, and not to the molecule as a whole.

Oil-soluble Phenol-formaldehyde Resins. (Chapter IX.) No published advances in this type have been made recently, but it may be assumed that the electrical properties follow the broad lines discussed under the thermo-setting and Novolak types, according to their chemical composition and behaviour under heat.

Urea and thio-urea resins (see Chapter IV). By the courtesy of Messrs. Beetle products the table below is given. The electrical characteristics of these materials are not as good as the phenol-formaldehyde compounds, but they are quite satisfactory for a number of purposes. One feature in which they show superiority is in the absence of 'tracking' or 'treeing'. The electric strength in the table is gauged in an empirical manner, using a proof test, and subjecting 1 mm. thickness of material to a constant voltage of 9,000 and determining the temperature at which breakdown occurs.

	<i>Beetle Industrial (Straight urea)</i>	<i>Beetle (Mixed thio-urea, urea)</i>
Temp. of moulding	140-145° C.	140-145° C.
Pressure of moulding	2,240-4,480 lb./sq. in.	3,360-5,600 lb./sq. in.
	The higher pressure being required for shapes having considerable lateral flow.	
Curing time	2-5 min.	3-7 min.
	Dependent on thickness and depth of moulding.	
	When properly cured mouldings should be ejected hot.	
Apparent density as packed	0.58	0.58
Specific gravity	Natural and colours 1.5	Natural and colours 1.49
	White and cream 1.54	White and cream 1.59
	Grade 'B' 1.45	
Tensile strength	5,500-7,500 lb./sq. in. cross-section	5,500-7,000 lb./sq. in. cross-section
Impact strength	Grade 'A' 5.2 kg./cm. ² Grade 'B' 4.5 kg./cm. ²	5.2 kg./cm. ²
Water abs. 24 hours	0.6	0.1
" " 7 days	2.5 per cent.	0.4 per cent.
Dielectric strength		<i>vide supra</i>
Temp. of breakdown at 9,000 volts A.C.	Grade 'A' 45° C. Grade 'B' 35° C.	60° C.
Volume resistivity, 15° C.	Grade 'A' 100×10^{10} $\Omega/\text{cm.}^3$ Grade 'B' 30×10^{10} $\Omega/\text{cm.}^3$	Natural and colours $1,000 \times 10^{10} \Omega/\text{cm.}^3$ White and cream $60 \times 10^{10} \Omega/\text{cm.}^3$
Surface resistivity	Natural and colours $35 \times 10^{10} \Omega/\text{cm.}^2$ White and cream $30 \times 10^{10} \Omega/\text{cm.}^2$ Grade 'B' 15×10^{10} $\Omega/\text{cm.}^2$	Natural and colours $170 \times 10^{10} \Omega/\text{cm.}^2$ White and cream $60 \times 10^{10} \Omega/\text{cm.}^2$
Coefficient of expansion	Natural and colours 0.000027/°C. White and cream 0.000027/°C.	Natural and colours 0.000028/°C. White and cream 0.000030/°C.

Alkyd resins. Cf. Chapter XI.

Butyl rubber. This material is being developed by the Standard Oil Company and applied to cable insulation. The following comparison with natural rubber has been published by the Esso Laboratories.²²

Pure natural rubber	water absorption	11.2-12.6 per cent.
" butyl "	" "	2.9 per cent.
Dielectric constant for 10,000 cycles:		
Pure natural rubber	2.11 dry; 2.11 after 88 hrs. in water	
" butyl "	2.46 " ; 2.76 " " "	

Polyvinyl plastics (see Chapter V). These compounds are considered as of considerable importance in the cable industry, according to Schatzel and Cassell.²³ They are stated to have a breakdown voltage of 1,000 volts per mil, but are subject to flow at 125° F. According to Patnode, Flynn, and Weh,²⁴ polyvinyl acetal is used for

wire enamel and is given as more resistant to abrasion, more flexible, and less affected by stretching than commercial wire enamels. It is also given as unaffected by solvents and as having a B.D.V. at room temperature of 8.8 kilovolts for the enamel coating against an average of 4–10 kilovolts for commercial enamels. After soaking in water 3.2 kilovolts was obtained against 2–8 kilovolts for commercial wires.

Polystyrol (see Chapter V). By the courtesy of Messrs. J. M. Steel & Co., Ltd., the table below is given.

A good sample of this product should possess the following constants:

(Loss Angle)	
Power loss tg	= $0.3-0.6 \times 10^{-3}$
Dielectric constant	= 2.99
Resistance, approx.	$10^{17} \frac{\text{ohm cm.}^2}{\text{mm.}}$

The values given are almost independent of temperature between 20 and 100° of the readings given.

Breakdown voltage at 100°	10.2 kv.
Ditto, after 240 hours' immersion in water	10.2 kv.

According to Matheson and Goggin,²⁵ the breakdown strength is given as equal to that of good mica, i.e. 5,500 volts per mil and after 48 hours' immersion in water 4,500 volts per mil. The water absorption is given as less than that of ebonite phenol fibre or cellulose acetate.

The dielectric constants and power factors at different frequencies are given below:

	Dielectric constant	Power factor
60 cycles	2.6-2.7	0.02
1,000 „	2.6-2.7	0.02
1,000,000 „	2.6-2.8	0.04

Softening-point given as 220–40° F.

Heat conductivity 3.2×10^{-4} cal./sec./cm./°C. In the Plastics Comparator²⁶ polystyrene is given a figure of 2 for dielectric strength, against a figure of 8 for heat-resistant phenolic resin.

Resistivity : polystyrene 2;	heat-resistant phenolic resin 8
Loss factor: polystyrene 1;	low loss phenolic resin 4

Schatzel and Cassell²³ say that polystyrene is too brittle for cable work, but mixtures of butadiene and polystyrene may be used.

Cellulose acetate (see Chapter II). Attempts have been made to use this for impregnating varnishes. These, however, have been only partially successful, which at first sight is curious, because the insulating characteristics are good. The viscosities of solutions are rather high and in consequence only low concentrations of solid matter can be used in order to get penetration, rarely more than 10 per cent. being permissible. These solutions are frequently modified by the addition of other ingredients in order to raise the concentra-

tion. Cellulose acetate has a dielectric strength of approximately 800 volts per mil. Its insulation resistance is high and it is very resistant to water and oil, although its specific inductive capacity assumes rather large values with very small quantities of moisture. According to Schering,²⁸ cellulose acetate has been used satisfactorily for impregnating varnishes for various kinds of small electric motors. It has not found much favour generally, because in bulk it is not very stable and under the influence of the electric field decomposition sets in, and the insulation fluctuates. It has been used **successfully as a wire enamel, it dries rapidly and evenly to an oil-resisting coating which is oil-proof and resistant to water and ozone.** For cable-finishing cellulose acetate holds a field peculiarly its own. It does not burn readily, being no more inflammable than paper, and this can be considerably reduced with many modern plasticizers. It dries rapidly and gives a good finish, as owing to its strong filming properties, and great contraction on drying, it pulls down the cotton fibres, leaving a smooth finish in contradistinction to the rough finish obtained by the use of most oil varnishes on untreated cotton.

Finch²⁷ comparing different dielectrics for condenser work gives the following table:

	<i>In. resistance</i>
Kraft paper plain 0.0011 in.	100 megohms/cm ³
" " impregnated wax 0.0013 in.	140 " "
" " " baking varnish, 1 coat 0.0015 in.	434 " "
" " " " " 2 coats 0.0025 in.	4,595 " "
Cellulose acetate 0.001 in.	70,000 " "

Cellulose acetate is not suitable for temperatures above 75°. Cellulose acetate was originally used for wire enamel, but is not now used.

Cellulose ethers (see Chapter II). We are indebted to Messrs. J. M. Steel & Co., Ltd., for the following information on their A.T. Cellulose Ether, which is given exactly as received.

The cellulose ethers have been found to be very suitable for different types of insulations. The following data were obtained from films containing 40 per cent. by weight of A.T. cellulose and butyl stearate.

Ageing at 100°—brittle after hours	100
Breakdown in air, normal kv.	13.2
Ditto, after immersion in water at room temperature:	
After 24 hours, kv.	11.4
After 48 hours, kv.	11.4
After 96 hours, kv.	11.4
Breakdown in Trafo Oil, kv.	18.2
Ditto, after immersion in oil at 100°:	
After 24 hours, kv.	20.0
After 96 hours, kv.	20.0
Dielectric constant	3.2
Dielectric loss, tan δ	6×10^{-13}
Resistance, M Ω	2×10^{12}

According to Schatzel and Cassell,²³ ethyl cellulose is the best of the celluloses for cable work.

Chlorinated diphenyls. One of these is apparently a very stable body of a syrupy nature and comes to swell the already very large and constantly growing group of plasticizers for the cellulose compounds. It has quite good electrical qualities and promises well. Others are solid resinous bodies which have good electrical properties; they are compatible with oils and are marketed under various trade names such as 'Clophen' and 'Arochlor' (Aroclor).

They are finding a satisfactory use as a cooling medium in transformers in place of oil, their high latent heat and non-inflammability, being important factors.

Sulphonamide resins. See chapter on Miscellaneous Resins, Chapter XIII, p. 351.

Acrylic acid resins. See Chapter VI.

CLASS II. NATURAL MATERIALS

Gilsonite. This is a black bituminous substance of the class of asphaltites, naturally occurring in Utah and Colorado. It has a solubility of over 90 per cent. in carbon disulphide, a specific gravity of slightly over 1.00 up to 1.10, and a melting-point of 250-350° F., measured by the K. and S. method. From a moulder's point of view it behaves well, takes filling material satisfactorily, assumes a fair polish, has reasonable flow in the mould, and leaves the mould clean. Its percentage of sulphur is low, usually less than 2 per cent., and this is well combined and has no deleterious effect on copper. As an insulator its characteristics are good; no published figures are available, so that only personal impressions from experience are given. This applies equally well to most of these natural products, as the electrical properties of these materials can be considerably altered according to treatment. The dielectric strength of Gilsonite is not very great in thin films, but increases relatively rapidly with increasing thickness, differing in this respect from the fixed oils which usually have a relatively greater dielectric strength in thin films than in thick ones. Its specific inductivity capacity is rather low, being usually under 2, and its specific insulation resistance is high. It possesses great chemical stability and water-resistance, both important features from an insulating point of view. It is, however, affected by oil, and should not be used where resistance to this material is required. It is possible to modify this feature by suitable treatment, but the general characteristics are thereby altered. The method of working this material is by pugging it in suitable heated mixers with the requisite proportion of filler until it is satisfactorily compounded, and then passing it through hot rollers, which convert it into slabs ready to be cut up and used direct in the mould. It will be seen from this that the ratio before and after moulding is practically the same, so that close moulds may be used for these compounds.

Glance pitch. This material may be said to run next to Gilsonite, but its quality is not nearly as uniform, and hence must be regarded

with more suspicion. It occurs native in Mexico, Colombia, South America, and in the West Indies. It is blacker than Gilsonite and is usually less soluble. It has a higher sulphur content, and the melting-point is approximately the same. Owing to its wide variations no useful purpose can be served by giving constants, but it is sufficient to say that the better qualities approach Gilsonite and even in some cases surpass it. Its variability, however, militates against it, every consignment needing careful checking.

Stearine pitches. These are residual products from the distillation of fatty acids, and their chemical and physical properties vary enormously according to their treatment. They are capable of giving very good results if properly used, but consignments need very careful watching, and in order to obtain satisfactory results they really need a preliminary treatment, in order to enable a start to be made from a comparatively uniform material. These disadvantages account for their unpopularity, despite the fact that the electrical properties of some grades are very good.

Petroleum, coal-tar, and wood-tar pitches. These materials are only used in the inferior grades, although the latter two have been used to produce types of thermo-setting compounds in conjunction with formaldehyde; for this purpose the pitches or tars must still contain some phenols. According to Schering,²⁸ good results have been obtained with coal-tar pitch by vulcanizing with sulphur.

Bituminous varnishes. Many excellent varnishes are made on a bituminous base. They possess good water-resistance, although in the main they are affected by transformer and lubricating oil. Nevertheless, varieties are produced which are entirely unaffected by hot transformer oil. In general they are good radiators of heat and their insulation temperature coefficients are good, the fall of insulation on rise of temperature being frequently very small, although occasionally there are some very bad examples to be met with. By the use of bitumen it is possible to produce varnishes which possess greater margins of safety than with almost any other materials. This explains their popularity for the insulation of heavily worked and highly rated coils operating at elevated temperatures. Bitumen, however, is such a comprehensive term that it must not be assumed that because a varnish is bituminous that it is of necessity good. For repair work, quick-drying varnishes made from gilsonite or glance pitch are in frequent use; such materials are affected by oil and should not be used where this is liable to be a disadvantage. Many so-called plastic varnishes are produced on a bituminous base, and these possess the property of self-healing any cracks produced by mechanical shock and exposure to low temperatures, the heat of working of the machine being sufficient to effect the necessary flow. All these bitumens, either alone or in combination, are used as solid compounds for impregnating electrical machinery. Care must be taken so to arrange the melting-point, that the fibrous insulation is not affected. Cotton begins to char at 225°, artificial silk at 198°, and natural silk

at 218°. Asbestos or glass coverings permit the use of very high melting-points.

Bitumens having a melting-point of about 80° are used in the manufacture of bituminized paper; this is usually marketed in two different thicknesses, one about 3 mils and one 7 mils thick. The breakdown strength of such paper is higher than that of the untreated paper would be; usually it will stand from 250 to 400 volts per mil when tested on alternating current for 1 minute.

The mechanical strength is much improved, *tensile strength* being 8–12 lb. per mil per in., and *bursting strength* (Ashcroft) 40–80 lb. per sq. in. for the 3-mil paper and 80–100 lb. per sq. in. for the 7-mil paper. The resistance to chemical influence is high and the ageing properties are very good. The impermeability to moisture is of quite a high order, and it is natural that such papers are finding wide applications. They possess the advantage of enabling one to stick them together by pressing with a hot iron, but, as this property might be detrimental on storage, such tendency to adhere is prevented by dusting the surface with French chalk or kaolin. Such papers are usually required to have a minimum of 30 per cent. bitumen and a maximum of 50 per cent., and a usual pass test for electric strength would be the application of 600 volts for 1 minute to the 3-mil paper or 1,000 volts for 1 minute to the 7-mil paper. The paper should not fail under these tests.

It should be borne in mind, however, that such bitumens will be soluble in oil, and care should be exercised to refrain from using them where this would be a disadvantage.

Fig. 44 shows an electrically heated impregnating plant. This has the advantage of dispensing with the drying out, necessary to remove the solvent employed in reducing the varnish to working consistency. It also results in a much more solid job, a greater quantity of insulator remaining in the coil, the interstices of the wire being more filled up, and the heat-dissipating qualities of the coil being improved. They have, however, in general the disadvantage that, since they are melted into position, they can also be melted out, and hence, unless a sufficiently high melting-point compound is chosen, they are liable to soften and be thrown out of rotating parts by centrifugal force.

Mineral rubber. Mid-Continental semi-asphaltic petroleums or Mexican petroleums are blown, either alone or after fluxing with gilsonite. Such compounds are called blown bitumens. Various patents have been taken out for blowing petroleum products with various catalysts, but it is general commercial present-day practice to blow these bodies without addition at a temperature of 550° F. for from 6 to 12 hours, using approximately 40 cub. ft. of air per min. per ton of compound treated. The compounds obtained in this manner are less susceptible to changes of temperature, but melt to more viscous liquids, and usually require higher temperatures in order to obtain a satisfactory pouring-point. These compounds can be used in the vacuum impregnating chamber, although they are somewhat

more sluggish in their penetration than the straight petroleum bitumens; on the whole, however, their performance is preferable.

Sulphurized bitumens. These petroleum residues can be modified by treatment with sulphur as well as by blowing, and the resulting products are very similar. Care should be taken, however, that no

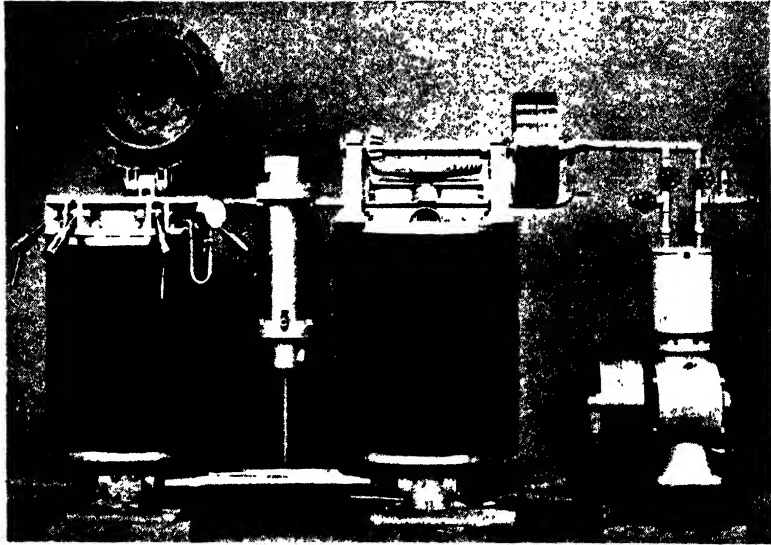


FIG. 44.

Electrically-heated impregnating plant (Messrs. George Scott & Sons).

active sulphur is left, as this will readily attack copper. Naturally the blown bitumens are preferred for electrical work, but where desired the presence of free sulphur can readily be detected by dissolving the bitumen in a suitable solvent, such as chloroform, and immersing a piece of brightly polished copper foil. It is advisable to keep the liquid warm during this test—about 50–60°—and maintain the concentration at about 2 per cent. of bitumen by occasional addition of solvent. Thirty minutes is usually sufficient to determine the presence of sulphur, which will be evidenced by a dark stain on the portion of the copper which was immersed.

Mineral waxes. According to Abraham,⁵³ this is: 'A term applied to a species of bitumens and to certain pyrogenous substances of various colours, viscous to solid consistency, having a characteristic lustre and unctuous feel, comparatively non-volatile, composed principally of saturated hydrocarbons, substantially free from oxygenated bodies, containing considerable crystallizable paraffins, sometimes associated with mineral matter, the non-mineral constituents being easily fusible and soluble in carbon disulphide.' Under this heading are ozokerite, ceresin, paraffin wax, and montan wax.

The characteristics of these bodies vary largely with the proportion of bitumen they contain. Ceresin and paraffin wax are the more waxy constituents and find use in the electrical industry mainly for impregnating condensers and small coils which are not subjected to any temperature rise.

Ozokerite and montan wax find use mainly for cable insulation, their suitability varying with the amount of bitumen present. They have comparatively sharp melting-points, melt to thin liquids which are easy to handle, and penetrate well. The cable is usually coated by drawing through a bath of the molten compound in a trough, and careful selection of the compound must be made to ensure that it slips easily through a die and gives a satisfactory coating, which shows no tendency to flake. Generally speaking, the more bituminous these bodies are the more suitable they are. They have good resistance towards chemical influences and are very suitable bodies for their purpose. The S.I.C. of a good bituminous montan wax is practically unaltered after 6 months' exposure to a solution of brine, a feature of great value in cable insulations.

Soft plastic compounds. Compounds of varying degrees of hardness can also be made by fluxing Manila and Pontianak resins with castor oil. This has the advantage of being insoluble in cold mineral oil and also of having no tendency to cause sludging. Soft compounds can be made in this way, and it is not uncommon to fill them by admixture with slate powder or some such similar material. Such compounds are used for sealing joints to render them oil-proof and for work of a similar nature in transformers and oil-cooled switchgear. The electrical properties of these resinous compounds are not of the best, and no great reliance is placed on them for insulation, the design of the machine usually taking care of this. The adherence to metal of all varieties, except the soft compounds, is poor, but this can be improved if the metal be first painted with shellac varnish. Certain plastic compounds are made with syrupy forms of phenol formaldehyde resins and fillers, but they are inclined to develop cracks after a time.

Wood pitches. The hard woods not of the Conifer type yield on distillation pitches which find a great field in the electrical industry. Careful selection is needed, but a correct pitch is hard and of glossy fracture, softens at 100° or just over, and yields nothing to hot transformer oil, being completely insoluble. They dissolve readily in acetone, melt to liquids which penetrate well and have good electrical properties, and show a high resistance to the influence of chemicals. They are produced principally in America and Russia. The American product frequently reaches a very high standard.

Bone pitch. This is sometimes used as an oil-resisting compound, but it is of a very variable nature. With careful selection good results can be obtained, but care should be taken to ensure that it does not contain too much free carbon. It is resistant to chemicals, and the adherence to metal of the softer kinds is fair.

Coal-tar pitch. The use of this material for machinery is not to

be recommended, but it finds quite a fair field for filling dry batteries and accumulators. A harder and mechanically more satisfactory compound is obtained by filling the pitch with about 30 per cent. of a solid powder such as chalk. If, however, the compound is to be used for accumulators the chalk should be replaced by something unaffected by sulphuric acid, such as barytes or strontium sulphate.

Coke-oven pitch, water-gas pitch. These materials are similar to coal-tar pitch, but owing to their being produced at somewhat higher temperatures they are analogous to the harder varieties of that material.

Tests. Bituminous filling compounds (excluding those used for cable boxes) have been arranged into five classes by the Electrical Research Association, based upon their dropping-points as determined by the ball and ring method.

<i>Class</i>	<i>Dropping-point, °C.</i>
I	less than 40 Fluid Grade.
II	above 40 but less than 70.
III	above 70 but less than 90.
IV	above 90 but less than 120.
V	above 120.

A suitable method of determination of electrical strength is being devised by the E.R.A., and in a proposed purchasing specification issued in May 1934, they recommend that the compound shall be stable and shall not emit excessive fumes when heated to the pouring temperature. On cooling there shall be no formation of either gas pockets or cracks. The compounds shall have no injurious effect on fibrous materials such as cotton, paper, or the like, nor on copper, brass, or iron at the service temperature. The compound shall be capable of being remelted repeatedly without the constituents separating out. The compound shall be free from coal-tar and coal-tar derivatives and free from water. Clauses for viscosity, pouring-point, flash-points for the various classes, freedom from acidity, and injurious sulphur, resistance to moisture, adhesiveness, penetration, &c., are given.

Hard rubber. This material is variously known as vulcanite, ebonite, or stabilit, and is made by treating rubber with sulphur under the influence of heat. The proportion of rubber to sulphur is one which has received attention from many workers who have studied this relationship and the effect of the sulphur content upon the properties. This vulcanized rubber may or may not be compounded with other ingredients, fillers, &c., according to requirements. It is usually made in the form of slabs or rods which can be worked to the shape desired on a lathe and sawn or tooled with ease. It finds very many applications as an electrical insulator, and but for two defects would have found much more universal use. Firstly, it is not very resistant to heat and is inflammable; secondly, it is affected by light, which causes an oxidation of the sulphur and the production of a conducting layer on the surface. These defects can be greatly minimized as, for instance, in keramot, stabilit, eisen-gummi, gummi-

asbest, &c., but the rapid rise of the phenol-formaldehyde resins in which these defects are practically absent has militated against the more widespread use of hard rubber.

Rubber/sulphur ratio. According to Glancy and his co-workers,²⁹ a rubber sulphur mixture during vulcanization rapidly increases in strength after passing a combined sulphur content of 23.5 (one atom of sulphur in each $C_{10}H_{16}$ group). The hard rubber rapidly increases in strength, approaching a maximum at a vulcanization coefficient of 40-2.

Cross-breaking strength. Esch and Heil³⁰ found that the breaking strain in three-point loading tests increased with the total sulphur content from 20 to 30, but decreased for higher proportions of sulphur. They used para-rubber stock with and without various amounts of hard rubber dust, each mixing being vulcanized to its best point.

Impact strength. Pearsall³¹ investigated the effect of combined sulphur on impact strength determined in three different ways:

- (1) A falling hammer method.
- (2) The Izod method.
- (3) The Charpy method.

Impact strength decreased continuously with the increasing sulphur content.

Plastic yield and yield temperature. Pearsall³¹ in the same article investigated the plastic yield of a mixing of smoked sheet 15, reclaim 30, hard rubber dust 32.75, carbon black 2, magnesia 0.25, pine tar 4, and varying proportions of sulphur. Each sample was vulcanized until less than 0.5 part of sulphur remained uncombined. He used a rising temperature method and found that an increase in vulcanization coefficient from 25 to 40 resulted in an increase of yield temperature from 58° to 74°. A further increase of vulcanization coefficient to 45 raised the yield temperature only 1° more.

Water absorption. Winkelmann and Croakman³² investigated the water absorption of a 71.5/28.5 rubber-sulphur mix, and showed that the water absorption decreased very rapidly as the optimum period of vulcanization was reached.

According to Demuth,³⁶ commercial loaded rubbers absorb more water than pure hard rubber.

Volume resistivity. The insulation resistance of rubber in increasing states of vulcanization has been investigated by Curtis, McPherson, and Scott,³³ the specimens being at a temperature of 25° C., and the relative humidity less than 1 per cent. They measured the volume resistivity after application of a fixed potential for a minute. They found that on changing the sulphur content over a range from 18 to 32 per cent. a sharp maximum resistivity of about 3.25×10^{16} ohms/cm.³ was observed at a combined sulphur content of 26.5 per cent.

Flight³⁷ and Wernicke³⁸ say mineral fillers lower the insulation resistance. Gottlob³⁹ says chalk is best.

Permittivity. Curtis, McPherson, and Scott,³³ in the article quoted

above, investigated rubber-sulphur mixings until less than 1 per cent. of sulphur remained. On measuring the permittivity at 25° and 1,000 cycles per sec. they found that this increased from 2.77 to 2.9 over a range of 19–32 per cent. combined sulphur, there being a minimum at 19 per cent.

A more complete investigation was made by Kitchin³⁴ at various compositions, temperatures, and frequencies. He found that the effect of combined sulphur on permittivity was small within the hard-rubber range and under most of the conditions employed.

He studied hard rubbers of 19.36, 22.57, and 28.41 per cent. of combined sulphur. The original paper should be referred to for complete details which are very full; see also Guthrie.⁵¹

According to Owen,⁴⁵ the permittivity may go up to 7 when loaded with mineral matter. The Cambridge Scientific Co.⁵² and Kühlewein⁵³ found that stabilite, a hard rubber heavily loaded with magnesia, had a permittivity of 4–6, while keramot, according to Anderson,⁵⁴ had a value of 4 at radio-frequencies.

Power factor. Blake and Boggs³⁵ found that for a frequency of 1,000 cycles there was very little effect of increasingly combined sulphur at low temperatures. At high temperatures, however, there was a considerable increase of power factor below a composition of 32 per cent. of combined sulphur.

Kitchin³⁴ showed that curves relating power factor and combined sulphur each exhibited a sharp maximum, the combined sulphur at which the peak occurred depending upon both the frequency and the temperature. Temperature increase or frequency decrease moved the position of the peak to higher combined sulphur. Mineral matter increases the dielectric losses.^{34, 35, 36}

Dielectric strength. Curtis, McPherson, and Scott³³ state that the breakdown strength of hard rubber is less dependent on rubber/sulphur ratio than on other factors.

The foregoing data show that there is as yet no satisfactory evidence on which to base opinions of the most suitable percentage of sulphur for all purposes, the general trend being in favour of the higher percentages. The influence of mineral filling agents is much more definite. Mineral fillers lower the breakdown strength. Siemens⁴⁴ gives good-quality Admiralty sheet 100 kv./mm., keramot, 55 kv./mm.

Rate of combustion. Schering²⁸ states that pure hard rubber burns briskly with a sooty flame, but vulcan-asbest and gummi-asbest, containing only 10 per cent. of rubber, burned with difficulty.

Tensile strength. Heavily loaded commercial hard rubbers, such as stabilite, vulcan-asbest, gummi-asbest, and eisen-gummi, have been investigated by various writers and in all cases the tensile strength has been found to be low.^{36, 37, 38}

Cross-breaking strength. Flight³⁷ and Wernicke³⁸ have both shown that the cross-breaking strength of heavily loaded commercial hard rubbers is less than that of pure hard rubbers.

Rubber. The application of rubber in the electrical industries is

of two distinct kinds: firstly, the partially vulcanized rubber such as is used for cable covering, and secondly the highly vulcanized hard rubber or ebonite which has been dealt with above. For cable covering rubber holds a unique position, but is seldom used as a final or top covering owing to the destructive effect of light. In consequence such cables are usually covered with braid which may or may not be further coated with some type of varnish or enamel. As distinct from gutta-percha and balata, pure raw rubber is never used by itself, but is vulcanized with up to 6 per cent. of sulphur. The proportion of sulphur may be as low as 1-2 per cent., and it is rare that cable covering is composed of this vulcanized rubber alone: softeners and fillers are usually incorporated in the mix. One of the most-favoured softeners is palm oil, though mineral oils, waxes, and bitumens are also used. For filling agents there are a number of substances which may be added, such as ground waste rubber, factis or rubber substitute, i.e. vulcanized oils, wood flour, and pulp, ground leather waste, ground fibres of various kinds, ground cork, &c. There are also a number of mineral constituents, such as kieselguhr, talc, barytes, whiting, magnesium carbonate, lithopone, &c. Colouring matter may also be added. The most common substances which help in the vulcanization are magnesium oxide and litharge and a number of organic accelerators.

Surface resistivity. According to Flight,³⁷ Schering,²⁸ and Demuth,³⁶ it would appear that loaded hard rubbers possess lower surface resistivity than do unloaded hard rubbers.

Surface deterioration in light. Most hard rubbers give a conducting film on the surface on exposure to light, and it has often been shown that this is acid. It has been supposed that this is produced by oxidation of the free sulphur, but some accurate work by Porritt and his collaborators^{40,41} has shown that the sulphuric and sulphurous acids which are formed on the surface of hard rubber when exposed to light and air, are produced through oxidation of sulphuretted hydrogen liberated through decomposition of the hydrocarbon/sulphur nucleus. This evolution took place in daylight, in the absence of free sulphur, water vapour, resins, or oxygen. According to Demuth, Franz, and Bergk,⁴² two commercial loaded hard rubbers, i.e. eisen-gummi and gummi-asbest, formed conducting films on the surface on exposure to light. One conflicting report is, however, obtained here, for Hartshorn⁴³ found that keramot, a hard rubber supplied by Messrs. Siemens, was comparatively little affected on exposure to sunlight, and also to ultra-violet radiation. The analysis of the material, according to Siemens,⁴⁴ is ash 28.08, total sulphur 17.94 per cent., free sulphur 0.47 per cent.

Gutta-percha and balata. These substances are allied to rubber, but as usually found in commerce they are associated with much more resin. Plantation rubber rarely contains more than 5 per cent. of resin, but both gutta-percha and balata may contain up to 60 per cent. of resin. These bodies are thermoplastics and are used principally in the cable industry for the insulation of submarine cables.

Gutta-percha was first suggested for this purpose by Michael Faraday and has proved so successful that it is still the main constituent of submarine cables to-day. For this purpose the Post Office standardize the percentage of resin present at 50 per cent. The quantity of resin can be modified by extraction with alcohol, in which some of the resin dissolves. Where it is required completely to deresinify these products, they are dissolved in petrol and then the solution is cooled, when the gutta-percha and balata are precipitated, since they are insoluble, the resin remaining soluble. Gutta-percha softens at 80°, but usually requires a temperature of 130° in order to work it in the bath through which the cables are drawn.

Dean⁴⁶ gives the table below:

	<i>Resistivity</i>	<i>Dielectric constant</i>
	ohms/cm. ³	
Leaf gutta-percha	100-500 × 10 ¹⁴	3
Tapped „ „	50-200 × 10 ¹⁴	2.9-3
Pahang „ „	2-300 × 10 ¹⁴	2.9-3.5
Bulongan red „ „	70-200 × 10 ¹⁴	< 3.2
Banger „ „	above 100 × 10 ¹⁴	< 3.2
Sheet balata	3-80 × 10 ¹⁴	3-3.3
Block „ „	4-300 × 10 ¹⁴	3-3.5
Paragutta	300-1,000 × 10 ¹⁴	2.6

Chlorinated rubber. This is claimed by certain makers to be perfectly stable, but experience must decide. It is certain that many unstable compounds have been offered for sale, and this fact has prejudiced the position. Chlorinated rubber is compatible with oils and its developments should be watched with interest. It is marketed under the names of 'Tegofan', 'Pergut', and 'Dartex'.

Congo copal. This material is very susceptible to moulding technique; extremely hard and durable mouldings can be made from it. It can be made to flow easily or with difficulty under heat, and to have great strength and resilience. While there are many ways of fluxing these resins, which vary with the individual moulders, one of the methods most widely favoured is by having the resin made up into varnish with linseed oil, and then using this to make up moulding matrices or powders. One of the difficulties in making moulding powders lies in the fact that it is essential to wet the grains of the filling material evenly with the bonding agent. While it may seem an attractive method to powder the resin and intimately mix it with the filler, this method does not produce satisfactory results, because of the extremely viscous nature of the resin and the difficulty of impregnating the powder, which is essential if homogeneous results are to be obtained. The use of these materials belongs to the older technique of the moulding industry, as modern synthetic resins are making it impossible for the older materials to survive. There are still, however, occasions on which their properties are an advantage, and one such that they possess over the phenol-formaldehyde type is that they are not subject to the defect of 'tracking'.

Some oil varnishes made from Congo copal are used for finishing varnishes, but their use is not favoured.

Manila. The remarks that were made on Congo copal apply equally well here, except that with the softer varieties of manila another possibility is opened up. These are soluble in methylated spirit and, in consequence, permit of moulding powders being made up direct from the resin without the introduction of linseed oil. Mouldings made from this resin are extremely resistant to transformer and mineral oil.

Pontianak copal. This resin has to be treated in the same way as Congo and is capable of giving good results which are more resistant to oil than that resin. Manila and Pontianak are used as oil-proof solid compounds, but are liable to considerable frothing. Methylated spirit solutions of Manila copal are used as finishing varnishes. Dielectric strength 200-300 volts per mil. Short-oil Pontianak varnishes are used as oil-finishing varnishes.

Shellac. This is probably the oldest material used for this purpose and it should come more correctly under the classification of thermo-setting resins, as it possesses this property to a very great degree. In view, however, of the fact that it is a natural resin, and, as normally produced, it possesses this property in only a partial degree, it has been included in this section. If it had not been for the attraction of commercial speculators, there is very little doubt that it would still be in quite good favour. Its fluctuations in price as a market commodity, however, have given a great stimulus to its competitors, and it has now lost ground that it will probably never recover. Great efforts are being made by the Lac Research Association to ensure it a new lease of life. They have set themselves the task of improving its water-resistance, speeding up its thermo-setting, and of finding a suitable plasticizer for it. Verman and Bhattacharya⁴⁹ find that on distilling shellac in vacuum the bulk of the resin polymerized to a spongy mass and the associated wax and another resin which is soluble in ether was distilled over. They suggest that the two types of resin exist in a physical combination in the crude lac. They succeeded by methods of extraction in removing the wax and the volatile resin, and found the resulting lac greatly improved.

We may look forward to the further progress of this work with some degree of optimism. At present we are concerned with the natural article as we have known it in the past. Nowadays it is not much used in the production of moulding powders, but still finds a useful field in the preparation of laminated material. This is not so much due to any inherent defect in this material for this purpose as to the fact that the newer moulding technique has grown up round the newer moulding materials, leaving the older materials to get along with the older methods. Thus shellac has had its field of utility limited to the production of laminated products, and for many years after the introduction of synthetic resins it held an undisputed sway in the building up of laminated mica, but this has now been challenged by the glyptal synthetic resins. Shellac has somewhat

better properties than the phenol-formaldehyde resins as ordinarily prepared, but the ordinary shellac of commerce is more affected by water. Its power losses are lower than almost any other resin known, and there is little doubt that even now, if a stable source of supply of the pure resin could be obtained, it would come into great use for wireless work. The following table published by Warren⁴⁷ gives comparisons between shellac on the one hand and synthetic phenol-formaldehyde resins on the other, when made up into laminated paper boards.

	<i>Synthetic resin</i>	<i>Shellac</i>
B.D.S. 0.125 at 90° C.	170-300	185-400
Water absorption	0.3-2.5	0.5-3.0
Density	1.1-1.3	1.42
Softening-point	over 150°	above 90°

Of recent years a shellac-coated paper has been marketed under the name of 'Akron', several varieties being offered—tissue and different thicknesses in sheets, strips, and rolls. These papers are of great use to any one wishing to build up their own laminated board or to stamp out washers or separators; a pack can easily be made up into the requisite thickness by heating with a hot iron, which causes the laminations to adhere. The strip is used for small transformers or for interleaving coil windings, &c., and can be used in place of tacky oiled cambric, having the advantage of not being subsequently affected by oil or varnish. Shellac makes a satisfactory finishing varnish, but it does not give as high a gloss as Manila copal.

Rubber resins. In the reclaiming of rubber and by extracting gutta-percha and Iquitos balata with petroleum spirit, resins are produced, the harder varieties of which can be used in cheap mouldings. These resins have not much to recommend them for this work, as they are mechanically weak and in consequence are often used in conjunction with other materials. A patent has recently been taken out by Craven,⁴⁸ which aims at hardening and raising the melting-point of these resins by oxidation.

CLASS III. THE CHEMICAL-SETTING MOULDING MATERIALS

This class at the moment is much smaller than those preceding, and is practically limited to the casein materials or articles prepared from dried milk. This is rendered insoluble by the action of formaldehyde, but still, however, remains very much swollen. It is very slowly dried, and shrinks down to a hard horny substance which is sold in sheets or rods and can be easily machined. There are many types, marketed under names such as 'Galalith', 'Erinoid', 'Lactonite', 'Lactoid', 'Dorcaline', 'Esbrillith', and 'Sicalite'. These materials possess the advantage of being highly resistant to heat and only burning with difficulty. They form useful insulators for base plates, low-tension rheostats, switches, fuse-boxes, &c., and are used for

many purposes where costly china insulators would have to be employed, as complicated special designs would have to be made, but these casein materials can be worked to shape on the bench.

RESULTS OF A TEST BY THE ELECTRICAL EXAMINATION BOARD

(Technical Staatslehranstalten of Hamburg)

Electrical Resistance and Strength of 'Galalith'

A. ELECTRICAL RESISTANCE

Referring to a die of 1 cm. square at 750-volt continuous current.

<i>Condition of Galalith</i>	<i>Blond</i>	<i>White</i>	<i>Black</i>	<i>Tortoise-shell Blond</i>	<i>Tortoise-shell</i>	<i>Medium value</i>
	300,000 Megohm	920,000 Megohm	70,000 Megohm	5,400 Megohm	144,000 Megohm	..
400 hours in the open air of 90 per cent. rel. humidity.	9,180 Megohm	6,870 Megohm	1,930 Megohm	9,650 Megohm	4 750 Megohm	abt. 6,000 Megohm

B. ELECTRICAL STRENGTH, CONDITION OF 'GALALITH'

Condition of Galalith: 400 hours in the open air of 90 per cent. rel. humidity.

<i>Thickness of sheets</i>	<i>Blond</i>	<i>White</i>	<i>Black</i>	<i>Tortoise-shell Blond</i>	<i>Tortoise-shell</i>	<i>Medium value</i>
4 mm.	5,000 eff. volt.	5,500 eff. volt.	2,000 eff. volt.	5,000 eff. volt.	3,000 eff. volt.	abt. 4,000 volt.
6 mm.	5,000 eff. volt.	6,000 eff. volt.	6,000 eff. volt.

IMPREGNATING AND FINISHING VARNISHES

In the design of electrical machinery it is usual to separate conductors by a continuous covering of cotton or silk, the insulating characteristic of the system being usually sufficient without further treatment, if the machine were to work continuously in a perfectly dry atmosphere. Such conditions do not, however, obtain in practice, and as fibrous materials are considerably hygroscopic, large quantities of moisture are absorbed and the insulation of the system considerably reduced. It is not often realized that cotton will absorb from 10 to 15 per cent. of water under conditions that would normally be considered quite dry. In order to prevent this, the fibrous insulation, which has been dried by heat and vacuum, is treated without further contact with the atmosphere, with what is called an impregnating varnish. The function of such varnish is to fill the pores or interstices of the fibre with a material which shall itself be an insulator, and at the same time be sufficiently resistant to moisture to prevent its ingress. Fig. 45 shows a horizontal impregnating plant by Messrs. Geo. Scott & Sons with the door open and the trolley for carrying the armature into the chamber, the varnish tank being

in the background. It is so customary to describe varnishes and many other materials as waterproof that it is not often realized that such a thing as a completely waterproof varnish does not exist, this term being purely relative. Water vapour will escape through rubber many times faster than will hydrogen gas. The ideal to be obtained is a varnish which will delay the ingress of moisture as much as possible, one that will absorb water only slowly, as it is mainly

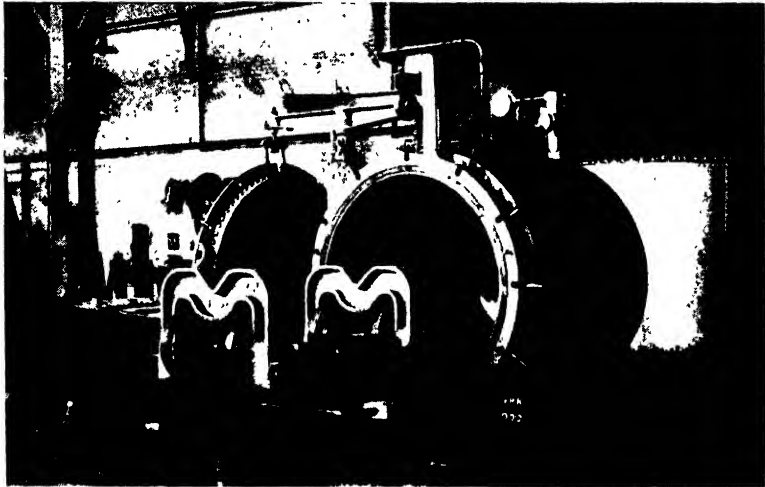


FIG. 45.

during the idle periods of the machine that it needs to be protected from moisture. The insulation resistance of dried cotton is very high, but its dielectric strength is rather low. The result of varnishing is to increase the dielectric strength and improve the factor of safety of the machine.

Frequently the insulation resistance is lowered as a result of varnishing, but with most varnishes used for this purpose this is such a small effect that it plays no important part, the finished value being of a sufficiently high order. These remarks are not meant to apply to the lowering of insulation due to varnishes containing methylated spirit, such lowering being of an entirely different character, and will be dealt with under 'Finishing Varnishes'.

One of the chief functions of varnish is to ensure that no great fluctuations in insulating value shall occur, and this is usually accomplished, provided sufficient care has been exercised in its selection. Varnishes for impregnation may be of three distinct kinds:

- (1) Resinous Varnishes. Shellac, bakelite, glyptals.
- (2) Oil Varnishes. Glyptals, phenol-formaldehyde, and natural resins.
- (3) Bituminous Varnishes.

RESIN VARNISHES

One of the oldest varnishes to be used for insulation is Shellac.

Shellac. This possesses many excellent characteristics, binding the coil well, and being unaffected by lubricating and transformer oils. It is still used to some extent nowadays, but is being gradually superseded by other materials. Its resistance to water is not of a very high order, but there is great hope that the pure lac which may one day be put on the market, as a result of work now being undertaken by the Lac Research Association,⁴⁹ may retrieve the bad name it has received in the past. The extremely low power losses of really good-quality lac will always be a valuable feature for instruments where efficiency is of prime importance, and the industry would welcome a stable source of supply.

OIL VARNISHES

Present-day oil varnishes are very different materials from the boiled oil which was the precursor of them. Many materials may be used in their manufacture, Congo copal, rosin, ester gum, linseed oil, and tung oil being the most usual materials of which they are composed.

Rosin or colophony. This material in one form or another enters into many oil-impregnating varnishes. It is rarely used in an unmodified form, as in this condition it is brittle and interferes very badly with the drying of the oil. If, however, its acidity is neutralized with glycerine (the so-called ester gum), or with metallic bases making the so-called rosinates, it produces an article of a much more satisfactory nature. If, now, these products be further combined with tung oil, very tough and satisfactory varnishes can be made.

There is no branch of the varnish industry which is more susceptible to technique than that of insulating varnish, and the snags of manufacture are so many that it is extremely rare for a varnish firm to take up this manufacture if they have not had previous experience of this business. Varnishes which would be perfectly satisfactory for exterior application would frequently be exceedingly dangerous if used for coil impregnation.

Oil varnishes. These varnishes form the bulk of the impregnating varnishes used. Their composition varies considerably, but they are nearly always a combination of linseed oil and China wood-oil, together with other modifying ingredients. When properly made they give bodies which dry well throughout the mass and are unaffected by transformer oil. One of the chief difficulties associated with linseed oil is the tendency to produce greening effects on copper. This 'greening' has been a very vexed question for many years, and it may be as well to develop the subject a little further. Any body of an acid nature will cause a green stain to appear on copper, and in the presence of cotton this stain will be readily absorbed, colouring the cotton green. If such acidic bodies be of low molecular weight

the salts formed will be poor insulators and may even cause a breakdown. If the action becomes localized on one spot it will be correspondingly more active, and in the case of thin wires may corrode through them. Greening may be due to a variety of causes and must not always be ascribed to varnish:

(1) *Cotton bleach*. It sometimes happens that the cotton covering of wire has not been properly washed and contains fair quantities of sulphates or chlorides which give rise to greening. A useful test to ascertain if there is any corrosive material in the cotton is to boil some of the wire, without troubling to detach the covering, in distilled water. Obtain a piece of perfectly clean copper foil and make a small dent in it about $\frac{1}{8}$ in. deep. Into this recess pour some of the extract from the wire and allow it to evaporate. If no green develops it may be taken that the cotton is free from bleach. It is best to renew the drop two or three times and set the foil aside for 2 days before drawing conclusions. When this test is positive there is no doubt, the green appearing in concentric rings.

(2) *Perspiration*. It is not every operative's job to handle wire, and it is frequently necessary to change a winder, because it is found that the wire they handle becomes 'verdigrised', especially in those spots where the wire has been held during a temporary stoppage of the machine. All sorts of precautions have been adopted to prevent this—gloves, rags, to hold the wire, dusting with French chalk, &c. It is best, however, to secure a suitable operative.

(3) *Soldering fluid*. The danger of greening from this source is well recognized in the electrical industry, and care is usually taken to ensure that only comparatively innocuous fluxes like rosin are used. It must, however, be pointed out that rosin itself will cause greening, although the compound produced, copper resinate, is quite a good insulator. The occurrence of green, however, is immediately viewed with suspicion, and in consequence it is advisable to use as little rosin as possible. It is not often realized that an insidious source of soldering fluid sometimes arises from the tin can in which the varnish is packed. Reputable makers of insulating varnish have realized this fact and use rubber-insert seamed cans and insist on a minimum of soldering and that this should be done with suitable fluxes.

Varnish. The foregoing forms of greening are all of a deleterious nature. The greening which occurs with varnish may be of two distinct kinds. Firstly, green compounds formed from high molecular oily or resinous acids present in the varnish. Such compounds are quite good insulators, and in consequence would not be detrimental. However, in view of the suspicion with which all greenness is regarded this type is rarely allowed to form. The acid value of the varnish is cut down to a minimum in manufacture, so that this type of greening is of very infrequent occurrence nowadays. When oils dry by oxidation volatile acids and aldehydes of low molecular weight are given off. In enclosed spaces and in the absence of free air these acidic bodies give rise to copper compounds, which are very poor

insulators. Where varnish has in the past been the cause of greening and subsequent breakdown, this is the type of effect which has led to the trouble. According to Fox and Penny,⁵⁰ in an investigation made on behalf of the Electrical Research Association, moisture is necessary to bring about corrosion. They further state that if the varnish film be such as to hinder movement of the copper compounds through the film, it is difficult to see how corrosion can spread. On the other hand, where the varnish does not dry properly, as sometimes occurs in the centre of the coil or on the varnished surface, corrosion may proceed rapidly, because the varnish is sufficiently fluid to permit of particle flow through its substance. It will be appreciated therefore that the internal drying of an insulating varnish is of fundamental importance. There are some excellent insulating oil varnishes on the market whose internal drying is of a very satisfactory order, and provided the coils are dried free from moisture before varnishing, no trouble should occur with standard makes of impregnating varnish. The normal procedure in many factories is to stove the windings (see Fig. 45) in the white, in order to dry out the moisture, then transfer them to the vacuum chamber, and subject them to a vacuum of about 28 in.; without breaking the vacuum, the cock connecting the varnish is turned on and the varnish allowed to run in until the coils are covered. The varnish cock is then turned off and pressure turned on to force the varnish into the coils. Next the varnish is drained off into the tank and the coils taken out and stoved until dry. The condition of dryness is judged by testing the coils with a megger, and when a sufficiently high value is reached stoving is said to be completed. In some factories vacuum impregnation is not adopted, but the procedure is much the same, the coils being first dried out and then immersed, whilst still hot, into the varnish tank and allowed to remain until bubbles cease to rise, which indicates that all air has been displaced. The coils are then drained and stoved. British Standards Specification No. 119 for Clear Baking Oil Varnish calls for a varnish which shall dry within 8 hours at a temperature of 95-100°, and shall then give a breakdown voltage of not less than 1,100 volts per mil for a thickness of 5 mils when tested at 90° C., or alternatively not less than 900 volts per mil for a thickness of 10 mils when tested at the same temperature. A limiting curve is given ranging from 2 mils to 17 mils and indicating the appropriate pass test voltage for the various thicknesses. An ageing clause states that no sign of cracking or decomposition shall be observed on varnished copper which has been subjected to 105° for 100 hours. Other clauses include finish, volatile matter, specific gravity, viscosity, resistance to moisture, acidity or alkalinity, effect of oil, and flash-point. Methods of conducting these tests are given, and whilst these abstracts have been published with the permission of the British Standards Institution, the original document B.S.S. 119 should be consulted for fuller details. Copies may be had from The British Standards Institution, 28 Victoria St., London. Price 2s. 2d. post free.

Thermo-setting oil varnish. There is at least one representative of this class of bodies marketed under the name of 'Durameg'. In this instance the thermo-setting does not depend upon chemical condensation as in the case of the phenol-aldehyde resins, but upon a somewhat new property of gelation. It has long been known that certain glycerides under the influence of high temperature will change over from a liquid to a solid condition. China wood-oil is a well-known example of this. The temperature of conversion in this case, however, is very high—500° F. or 260°—and is quite inadmissible for electrical apparatus. It is claimed, however, by the manufacturers of Durameg that they have succeeded in reducing this conversion temperature to 220° F. or 105°, a quite normal figure for the stoving of electrical apparatus.

CLOTH VARNISHES

Varnishes for the manufacture of electrical cloth and binding tapes may be of three distinct kinds or classes: the Tacky, the Dry Yellow, and the Bituminous.

Class I. May be either yellow or black and include the so-called Friction Tape or Insulating Tape. This class is mainly compounded with treated rubber, rubber resins, gutta-percha, soft coumarone resins, &c., sometimes on a base of previously varnished cloth.

In the case of the black, Stockholm Tar and Swedish Pitch may be used in conjunction with the rubber-base compounds.

Class II. These are oil varnishes with the addition of suitable resins, and their properties are covered by a British Standards Specification No. 419, which is for the finished cloth and includes mechanical strength tests, ageing and electrical strength tests. The mechanical strength tests include tensile strength along the warp and the weft for straight-cut cloth, and also tensile strength tests for bias-cut cloth, minimum pass figures being given. Tearing strength: minimum pass figures are given for a double tear, for both warp tear and weft tear. Ageing: this test requires that the varnished cloth, after having been artificially aged by being heated in an oven maintained at 110° for 24 hours, shall not have deteriorated more than 60 per cent. in bursting strength, the test to be conducted before and after ageing on the cloth brought to a uniform condition of humidity in a conditioning chamber. Electrical tests include a breakdown strength test at 90°, this being in the nature of a minute proof test, minimum values being given, and an electric strength test at 20° under tension, carried out on a bias-cut strip, which is also a minute proof test and minimum values are given. There is also a 'Highest Maintained Electric Stress' test. Again this is in the nature of a proof test, the minimum value being 60 volts per mil computed on a pack of 30 mils, the temperature of test being 90°.

For fuller particulars the original specification should be consulted, the above having been abstracted from it with the permission

of the British Standards Institution, 28 Victoria St., London, from whom copies can be obtained, price 2s. 2d. post free.

Class III. The above specification deals also with the black or bituminous cloth for the same purpose, minimum values being given and the same tests applied.

Technical report L/T 44 of B.E.A.I.R.A. shows that the permittivity and power factor of varnished cloth at low voltage gradients was independent of the voltage for all voltage gradients less than a critical value.

Conclusions:

- (a) When varnished cloth is subjected to an alternating voltage gradient less than a certain critical value, the power dissipated in the material is proportional to the square of the applied voltage, and the permittivity and power factor are independent of the voltage. The critical voltage gradient is less than 2 kv./mm.
- (b) The power dissipated under such conditions in the frequency range 50–8,000 cycles may be entirely accounted for by the phenomena of dielectric 'absorption' and conduction, and there is no discrepancy between direct and alternating current, provided the D.C. observations are made after times of charge or 'electrification' of the same order as the periodic time of the A.C.
- (c) The properties of the material are largely determined by its moisture content.
- (d) The power loss increases with rise of temperature, roughly exponentially. The rate of increase is of the order of 3 per cent. per 1° C., and there is some evidence that it is greater for the loss due to normal conduction than that due to absorption, especially when the moisture content is high. When the moisture content is low the power loss is much smaller, and increases less rapidly with rise of temperature.

SLEEVING AND CABLE FINISHES

The same varnishes with various modifications are employed for the production of varnished sleeving or for finishing cables covered with plaited cotton fabric.

WIRE ENAMELS

Oil varnishes suitably modified are also used in the enamelling of bare copper wires. The dielectric strength is frequently of a very high order and the mechanical strength good. All these materials, cloth, sleeving, and wire, are coated by drawing through a bath and then on through a stove to effect drying. From there the work goes on to a roll and is wound up ready for use. The process is a continuous one, the speed of travel being regulated by the time necessary to effect drying in the stove. Sleeving is usually done in yard lengths, as

it is not possible to wind it on a coil as with cable (see also pp. 392-4, i.e. polyvinyl acetal and cellulose acetate).

FINISHING VARNISHES

The varnishes are used for producing glossy oil-proof surfaces on coils and are usually made in two colours, amber (or golden) and black. It is usual to obtain these colours with dyes, although some of the blacks are produced with the aid of pitches such as bone pitch, hardwood pitch, &c., which are unaffected by oil. The resins used may be shellac, phenol-formaldehyde, manila copal, sandarac, accroides, &c., and are usually alcohol-soluble materials, although certain types of oil-soluble substances are also used.

OIL-FINISHING VARNISHES

In order to obviate the lowering of insulation resistance attendant on the use of methylated spirit various forms of oil varnishes are used. The resins used for this purpose should preferably be the oil-resisting ones, hard Manila and Pontianak copal being usual, and these are made up into short oil varnishes with linseed oil. Other types are quick-drying wood-oil varnishes, the amber colour being produced with dyes, and the black by the use of oil-resisting pitches such as bone pitch or Manjak.

In a proposed purchasing specification published by the British Electrical and Allied Industries Research Association, Technical Report, Ref. A/S 41, 1935, two types of finishing varnishes are recognized: Type I varnish with methylated spirit solvent to dry in 2 hours, and Type II varnish with non-alcoholic solvent to dry in 6 hours. The drying time is determined by the non-adherence of filter-paper pressed on the surface by a cylindrical 1 lb. weight. For further particulars see the above report or apply to the British Standards Institution, 28 Victoria St., London.

REFERENCES

1. S. Whitehead, *Dielectric Phenomena; Break-down of Solid Dielectrics*, Benn (1932)
2. Schering, *Z. für Instrumenten*, 1920, 40, 124; *Arch. für Elektrotechnik*, 1920, 9, 30; 1922, 11, 109; 1927, 18, 248.
3. P. Debye, *Physik. Z.*, 13, 97.
4. Turner and Hobart, *The Insulation of Electric Machines*, Whitaker & Co.
5. E. B. Wedmore, *World Power*, 10 Dec. 1928.
6. Director of Research, Technical Report L/T 26, E.R.A., *Theory of Break-down of Insulation through Thermal Instability* (1928).
7. J. A. Dellinger and J. L. Preston, U.S. Bur. of Standards, *Scientific Papers*, 1923, 19, 39.
8. W. S. Flight, The effect of Heat on the Elastic Strength of some Compound Insulating Materials, *J. Inst. Electric Eng.*, 60, no. 306, p. 218.
9. Harvey L. Curtis, *Insulating Properties of Solid Dielectrics*, Bulletin U.S. Bur. of Standards, 11 (1914-15).
10. L. Hartshorn and E. Rushton, 'Elect. and gen. Phys. Properties of Plastics', *Chem. and Ind.*, 1940, 59, 237.
11. S. Whitehead and Nethercot, *Proc. Phys. Soc.*, 47, 934.
12. L. Hartshorn, 'Dielectric Properties of Varnished Cloth', *Inst. Elec. Engrs.*, April 1932, 70, No. 424.
13. Güntherschulze, *Z. Elektrochem.*, Sept. 1927, 33, 60.
14. E. B. Wedmore, Preface to *Dielectric Phenomena*, 11, by S. Whitehead (1928).
15. Schumann, 'Dielectric Phenomena', *Z. techn. Phys.*, 1925, 6, 430.
16. S. Whitehead, *J. Oil Col. Chem. Assoc.*, 1931, 14, 307 (discussion).

17. J. L. R. Hayden and C. P. Steinmetz, *Electrical World*, 21 Oct. 1922.
18. Monkhouse, *Electrical Insulating Materials*, Pitman 1926.
19. B.E.R.I.R.A., report I/T 41.
20. B.E.R.I.R.A., report F/T 12.
21. B.E.A.I.R.A., report L/T 114.
22. *Ind. Eng. Chem.*, 1940, 32, 1283.
23. R. A. Schatzel and G. W. Cassell, *Ind. Eng. Chem.*, 1939, 31, 945.
24. W. Patnode, E. J. Flynn, and J. A. Weh, *Ind. Eng. Chem.*, 1939, 31, 1063.
25. L. A. Matheson and W. C. Goggin, *ibid.*, 1939, 31, 334.
26. Gordon Brown, *British Plastics*, 1940.
27. J. M. Finch, *Ind. Eng. Chem.*, 1940, 32, 1021.
28. Schering, *Die Isolierstoffe der Elektrotechnik* (Julius Springer, Berlin, 1924).
29. W. E. Glancy, D. D. Wright, and K. H. Oon, 'Rate of Combination of Sulphur with Rubber in Hard Rubber', *Ind. Eng. Chem.*, 1926, 18, 73; *R.A. Lond.*, 1926, 7, 106.
30. W. Esch and A. Heil, *Manufacture of Rubber Goods*, p. 216 (London, 1919).
31. D. E. Pearsall, 'Influence of the Sulphur/Rubber Ratio on the Physical Properties of Hard Rubber', *I.R.W.*, 1927, 77, 70; *Rubber Chemistry and Technology*, p. 137 (April, 1928).
32. H. A. Winkelmann and E. G. Croakman, 'Water Absorption of Rubber Compounds', *Ind. Eng. Chem.*, 1930, 22, 1367.
33. H. L. Curtis, A. T. McPherson, and A. M. Scott, *Density and Electrical Properties of the System Rubber-Sulphur*, Part II. *Electrical Properties of Rubber-Sulphur Compounds*. U.S. Bur. Sta. Sci. Pap. No. 560 (1927).
34. D. W. Kitchin, 'Dielectric Constant and Power Factor of Vulcanized Rubber', *Ind. Eng. Chem.*, 1932, 24, 549.
35. C. R. Boggs and J. T. Blake, 'Theory of Vulcanization of Rubber', *Ind. Eng. Chem.*, 1930, 22, 748.
36. W. Demuth, 'Solid Insulating Materials in Electrical Eng.', *V.D.I.*, 1927, 71, 1561.
37. W. S. Flight, 'Use of Rubber Products as Dielectrics', *Inst. Rubber Ind. Year Book*, 1923, 2, 386, and *India-Rubber J.*, 1923, 65, 967, 1007.
38. K. Wernicke, *Die Isolierstoffe der Elektrotechnik*, p. 94 (Brunswick, 1908).
39. K. Gottlob, *Technologie der Kautschukwaren*, p. 289 (Brunswick, 1925).
40. J. D. Fry and B. D. Porritt, 'Preliminary Investigations on the Causes of Deterioration of Ebonite when exposed to Air and Light', *India-Rubber J.*, 1929, 78, 307.
41. B. D. Porritt and D. M. Webster, 'Experiments on the Causes of the Deterioration of Ebonite when exposed to Air and Light', *ibid.*, 1930, 79, 239.
42. K. Bergk, W. Demuth, and H. Franz, *Die Materialprüfung der Isolierstoffe der Elektrotechnik*, p. 174, Berlin (1923)
43. L. Hartshorn, 'Surface Resistivity Measurements on Solid Dielectrics', *Proc. Phys. Soc.* 1930, 42, 300.
44. Siemens Bros., Ltd., Siemens' Ebonite Pamphlet (1926).
45. W. D. Owen, 'Synthetic Resins and Other Industrial Plastics', *Brit. Plastics*, 1931, 3, 97.
46. J. N. Dean, *Ind. Eng. Chem.*, 1939, 31, 699.
47. H. Warren, *Electrical Insulating Materials* (London, 1931).
48. A. B. Craven and the Yorkshire Dyeware and Chemical Co., Ltd., B.P. 278, 922.
49. L. C. Verman and R. Bhattacharya, *London Shellac Research Bureau, Technical Paper*, No. 1, 1934.
50. J. J. Fox and E. Penny, *Greening of Copper Wire*, B.E.A.I.R.A. Tech. report A/T. 54.
51. *The Blue Book*, Benn (1933)
52. G. E. Haefely, *Chem Ind.*, 1941, 16.
53. H. Abraham, *Asphalts & Allied Substances*, D. van Nostrand Co., New York, 1929, 3rd Edn.
54. Cambridge Scientific Inst. Co., Ltd., *Tests on Insulating Materials with the Cambridge L. T. Schering Bridge*. Pamphlet.
55. H. Kühlewein, *Z. techn. Physik*, 1929, 10, 280.
56. W. Anderson, *Phil. Mag.*, 1932, 7, 13, 986.

CHAPTER XV

THE PROBLEMS OF RESINIFICATION. I

By R. S. MORRELL

THE significance of molecular structure in relation to the properties of resins has been recently discussed by R. V. V. Nichols and P. Larose.¹ Most resins consist of macromolecules, i.e. long, flexible, chain-like structures of high molecular weight existing in independent units or bonded together in a single tri-dimensional lattice, the structure units of such molecules numbering hundreds and even thousands. The investigations of Staudinger have shown that some 50-100 structural units are necessary for the appearance of resinous properties; likewise the investigations of Carothers have shown that at least 100 or a molecular length of 1,000 A. are necessary to give the resin fibre-forming properties.²

Since most synthetic resins are produced by processes of polymerization or condensation, not only are simple long chains obtained, but where the starting materials contain medial double or triple bonds, or they contain tri-functional molecules (cf. p. 439), there may be formed cross-linkages between the chains or the development of branch chains. The constituent atoms may rotate about single bonds, and this freedom of motion tends to disorganize the molecule; but coupled with an attraction between the atoms or groups of atoms attached to the chain, the molecule may tend to wrap itself into helix form (cf. proposed helix form of synthetic rubber, p. 325). This aspect is worthy of consideration because a great number of resin systems must be built up in this manner. Within the molecules there are chemical forces represented by primary and secondary valencies, and within the resin-mass there are other forces (van der Waals and dipolar) produced by steric effects (i.e. effects due to the configuration of atoms or groups of atoms) and interlacing of the molecules. Nichols and Larose continue in their summary (loc. cit.) by pointing out that some of the characteristic properties of resins related to the concept of macromolecular structure are tensile strength, thermal behaviour, and pliability, i.e. elasticity. The tensile strength of resins is improved by orientation along parallel axes, in which position both chemical and physical forces have a maximum effect. The *thermo-plastic* resins have long-chain molecules with a few cross-linkages, softening on heating and setting on cooling, the cycle being capable of repetition. The *thermo-setting* properties are connected with bridge-linkages between the molecules. Both types decompose on heating, whereby it is concluded that the cross- or bridge-linkages between molecules are mechanically stronger than the forces between the atoms of the chain. The property of pliability or elasticity is related to the organization of the molecule. The helix formation, represent-

ing extreme disorganization, resists attempted organization by an elastic force. Cross-bonds between helices favour a more rigid structure and so reduce elasticity. The properties of the resins are also affected by the type of skeletal linkage and the substituent groups present. The C-C linkage between the molecules imparts water-resistance and dielectric strength. The ester linkages (as in alkyds) and the amide linkages (as in polyamides) are susceptible to hydrolysis and will not be stable in strong alkalis. Substituent chlorine atoms (as in polyvinyl chloride and chloroprene) give extreme chemical resistance, whilst the phenyl groups (as in polystyrene), being large, will reduce elasticity through steric hindrance.

H. Mark,³ in discussing the aspects of high polymeric chemistry, indicates the important variables in polymers affecting their technical applications. The variables are: (a) The chemical nature of the monomeric material, e.g. aromatic or aliphatic hydrocarbons, esters, a chloride or a ketone. (b) The average length of the main valence chains in the polymer depending on the method of polymerization at high or low temperatures, or the nature of the catalysts, &c. (c) The internal flexibility of the main valence chains. Long chains have internal mobility due to free rotation about single valence bonds; the mobility is reduced by substituents, rings, double bonds, &c. The flexibility of cellulose is very low; polyvinyl alcohol is medium, and polybutene is very high. (d) Cross-linkages give resistance to heat, impact, and abrasion, but cause increase in density and viscosity.

He introduces a new term *Vernetzungszahl* (netting number or index), to indicate the cross-linkages in the molecule, e.g. the netting number of *three* means three cross-linkages to 100 chain-linkages. The table on p. 418 shows the presumed netting numbers of polymers and the relation between the technical properties of the polymers and structure under the headings (a), (b), (c), and (d) given above.

In accordance with this table, a material of high heat, water, and electrical resistance and of high impact strength must be a hydrocarbon with long chains (flexibility immaterial) and strong 'netting'. A rubber-like material requires long flexible chains with not too much 'netting'. If it is to be oil-resistant, methyl groups must be avoided, and the two quantities of oil-resistance and high reversible elasticity require opposite factors. It will depend on whether oil-resistance or high elasticity is more important, and the choice will fall on the 'netting' number in favour of the more valuable quality. In the case of artificial rubber, the range of reversible elasticity must not be very high (about 100 per cent.), but the abrasive strength and oil-resistance are so important that a considerable degree of 'netting' is preferable. In the case of neoprene, buna, or thiokol there is a considerable degree of 'netting'.

The attempt made by Mark to correlate structure with technical properties is of great interest, although the conclusions are as yet of very limited application, and any rules laid down must be preliminary and imperfect.

	Heat-resistance		Oil-resistance		Water-resistance		Impact strength		Abrasive strength		Reversible elasticity	
	Decreased	Increased	Decreased	Increased	Decreased	Increased	Decreased	Increased	Decreased	Increased	Decreased	Increased
(a)	*	*	by CH_3 , OCH_3 and fatty groups	by OH and O bridges	by OH, NH_2 , OCH_3 , HSO_3 and COOH groups	by CH_3 , C_6H_5 and fatty groups	*	*	by CH_3 or fatty groups	by OH groups	*	*
(b)	by short chains	by long chains	*	*	*	*	short	long	short	long	short	long
(c)	†	†	by very flexible chains	when chains not too flexible	very flexible chains	rigid chains	*	*	*	*	rigid chains	very much by flexible chains
(d)	low n.i.	very much by high n.i.	low n.i.	very much by high n.i.	very low n.i.	high n.i.	low n.i.	very much by high n.i.	low n.i.	very much by high n.i.	very much by high n.i.	low n.i.

* Means that this particular variable has little effect on the n.i. (netting index).

† Means that this particular variable has no effect on the special property (a), (b), (c), or (d).

Approximate Average Chain Lengths (b)

	<i>Degree of polymerization, i.e. number of monomers in the chain</i>
Natural rubber	approx. 500-1,000
Masticated cold rubber	" 50-200
Low polymerized styrene	" 50-100
Medium polymerized styrene	" 200-800
High polymerized styrene	" 2,000-500

Internal Flexibility of the Chains (c)

Cellulose	very low	Polyvinyl alcohol	medium
" esters	"	Polyisoprene	high
Polystyrene	fairly low	Polybutadiene	very high
Polyvinyl chloride	"	Polybutylene	"
Acrylic ester	medium		

Netting Indices of Polymers (d)

<i>Substance</i>	<i>'Netting' Index</i>	<i>Substance</i>	<i>'Netting' Index</i>
Native cellulose	nearly zero	Soft rubber	medium (5-10)
Native rubber	"	Polybutadiene	" (5-10)
Polybutylene	very low (3-5)	Hard rubber	high (10-20)
Polyvinyl chloride	" (3-5)	Buna	" (10-20)
Polystyrene	" (3-5)	Bakelite	very high (50)

Nichols and Larose⁴ point out that since resins are bought and sold on the basis of properties the chemist must know the relation between structure and properties. The chemist has at his disposal means to control the structure of synthesized molecules, such as selection of reactants, variation of their relative proportions, their concentration in diluents, the temperature of the reaction, and the type and concentration of catalysts. The ideal resin should have the following properties: it must be colourless, lustrous, hard, tough, strong, flexible, adhesive, of suitable solubility and softening power, with high electric insulating power, light, stable, non-inflammable, waterproof, chemically resistant, and with low cost. For these many reasons it is of the greatest importance that the causes of resinification should be explored. The factors of polymerization must be considered, as well as their connexion with the composition and structure of the active substances.

The important types of polymers are:—(1) *Homopolymers*. In which the molecules are built up of recurring units, e.g. polyethylene or vinyl resins, including polyethylene, polystyrene, polyisobutylene (polybutene), polydihydronaphthalene, polyindene, polycumarone, polyvinylchloride, polyacrylate, polymethylacrylate, polyacetylene type, e.g. polyacetylene and vinylacetylenes; polydienes, e.g. polybutadiene, polychloroprene, and polyisoprene. (2) *Heteropolymers* (co-polymers). Where unlike units are associated, as in the polyethy-

lenes or the vinyl resins, e.g. polyindene-coumarone and polyvinyl chloride-acetate; polyethylene-diene type, e.g. polystyrene-butadiene, polyacrylic-nitrile-butadiene. (3) *Hetero-condensates*, where the polymerization depends on association of units formed by interaction of two substances and elimination of water, as in the case of the alkyd resins, of sodium chloride in the case of polysulphide resins, polyalkylene sulphides, polyphenylethanes, phenolic resins, alkyd resins, urea-formaldehyde resins, polyamides, and the polyalkylene sulphides.

THE PROBLEMS OF POLYMERIZATION (HOMO- AND HETERO-POLYMERS)

The manifold applications of polymerization have required a systematic presentation of the chemistry involved. This has been dealt with in a treatise by R. E. Burk, H. E. Thompson, A. Weith, and I. Williams entitled *Polymerization and its Applications in the Fields of Rubber, Synthetic Resins and Petroleum* (American Chem. Soc. Monograph Series, 1937).

A general review of the above book has been furnished by R. E. Burk,⁵ and an abstract of that paper, with others, will provide the salient points for a general discussion on the problems of polymerization of resin-forming materials. The relationship between polymerization and molecular structure of hydrocarbons (homopolymers) will be summarized first.

Polymerization in its industrial applications may be defined as the combination of a number of molecules to form a single molecule in which the latter is bound together with the conventional chemical bonds.⁶ It must be pointed out that the causes of resinification are not dependent solely on the interaction of conventional chemical bonds, but this aspect will be further discussed later.

Table I shows the influence of the type of unsaturation on polymerization tendencies.

TABLE I

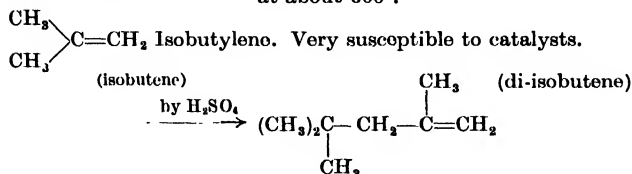
$H_2C=CH_2$ (Ethylene)	Stable at 150°.
$HC\equiv CH$ (Acetylene)	Stable at 150°.
$CH_2=CH-CH=CH\cdot CH_3$ (Pentadiene-1, 3 or Piperylene)	Polymerizes 68% in 15 days at 150°.
$CH_3-CH=C=CH\cdot CH_3$ (Pentadiene-2, 3 or sym. Dimethylallene)	Polymerizes in 4-5 days at 150°.
$H_2C=CH-CH=CH_2$ Butadiene-1, 3 or Erythrene	Completely polymerized in sealed tube in 10 days at 150°.
$HC=C-CH_2-CH_2-C\equiv H$ (Hexadiyne-1, 5 (Dipropargyl))	Polymerizes rapidly at room temperature.
$H_2C=CH-C\equiv C-CH=CH_2$ (Hexadiene-1, 5-yne-3 or Divinylacetylene)	Polymerizes readily at 80°.
$H_2C=CH-CH=CH-C\equiv C-CH=CH_2$ (1, 5, 7-Octatriene-3-yne or Acetylene tetramer)	Boils with polymerization at 40° (20 mm.).
$H_4C=CH-CH=CH-C\equiv CH$ (Hexadiene-1, 3-yne-5 or Acetylenediviny!)	Very readily polymerized.
$H-C\cdot C\equiv CH$ (Butadiyne-1, 3 or Diacetylene)	Polymerization rapid at 0°.

Table II shows the influence of alkyl substituents on polymerization tendencies.

TABLE II

Olefines

H₂C=CH₂ Ethylene. Polymerization at atmospheric pressure becomes rapid at about 600°.

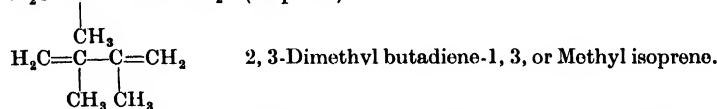


Conjugated diolefines.

H₂C=CH-CH=CH₂ (Butadiene-1, 3)

Difference is slight.

H₂C=CH-CH=CH₂ (Isoprene)



Vinyl-methyl-ketone: CH₂=CHCOCH₃—polymerized easily by 3,000 A.

Isopropenyl-methyl-ketone: CH₂=C(CH₃)CO·CH₃—less readily.

Table III shows the effect of halogen substitution on the polymerization of unsaturated compounds.

TABLE III

CH ₂ =CH ₂	Polymerization very slow.
CH ₂ =CHCl	Rapid polymerization.
CH ₂ =CCl ₂	" "
CHCl=CCl ₂	Polymerization very slow.
ICl=Cl	Polymerizes readily, explosive.
R-C=C-halogen	Stable when R is saturated.

Conjugated Diolefines (after Carothers)

Position and nature of substituent			Relative rate	Position and nature of substituent			Relative rate
	C=C-C=C			C=C-C=C			
	Cl	Cl	2,000	CH ₃	Cl		30
	I		1,500	C ₂ H ₅	Cl		30
	Br		1,000	C ₃ H ₇	Cl		10
	Cl		700	C ₂ H ₅	Cl		10
	Cl	CH ₃	500	Cl			7
Cl	Cl	Cl	120	CH ₃	CH ₃	Cl	1.5
				CH ₃			1

Table IV shows the effect of substitution on the polymerization of 1, 3-butadiene.

TABLE IV
Effect of Phenyl Substitution on the Polymerization of 1, 3-Butadiene

Position of substituent				Remarks
C=C—C=C				
C ₆ H ₅ C ₆ H ₅	C ₆ H ₅	CH ₃ C ₆ H ₅		Polymerizes 80 times as fast as isoprene. Polymerizes rapidly. Cannot be prepared in monomeric form. Polymerizes rapidly.
	C ₆ H ₅ C ₆ H ₅	C ₆ H ₅ C ₆ H ₅	C ₆ H ₅ C ₆ H ₅	
(C ₆ H ₅) ₂			(C ₆ H ₅) ₂	Can be polymerized only by powerful catalysts. Has not been polymerized.

Table V shows the nature of the catalysts used in polymerization.

TABLE V
Chief Catalyst Types which have been found effective for Polymerization

Type of Compound.

Metals: alkali and alkaline earths, copper, iron, platinum.

Acids: sulphuric, acetic, hydrochloric, hydrofluoric, phosphorus oxy-acids (in order of use).

Halides: aluminium (including aluminium fluoride), boron, zinc, antimony, copper.

Oxidizing agents: peroxides, oxygen, persalts.

Oxides: silica, alumina, copper, iron, zinc, manganese, molybdenum.

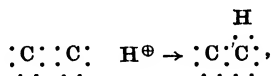
From the Tables I-IV given, the following conclusions may be drawn:

- (1) Hydrogen atoms on the unsaturated linkage are necessary for polymerization. An apparent exception is formed by halogen substituted acetylenes.
- (2) Increase in mol. wt. eventually reduces polymeric tendencies. Flory⁷ states the contrary in the case of polyester formation, in spite of decreased steric factors and decreased velocities which would be expected as the polymer grows.
- (3) Substitution of certain groups, e.g. halogens, vinyl, phenyl, acetylene, carbonyl, and ester groups, greatly stimulate the polymerization of unsaturated hydrocarbons.
- (4) The effect of substituents depends on their nature, number, and position as defined in the following generalizations.
- (5) Conjugated unsaturation leads to pronounced polymerization tendencies if too many hydrogens be not substituted.

- (6) Widely separated unsaturated groups approach in their polymerization tendencies those of the separate groups. (In some cases rearrangement to a conjugated form occurs.)
- (7) Non-aromatic ring structure containing unsaturation in the ring may have the unsaturation conjugated with side-chain unsaturation. Where the ring is aromatic, carbon-carbon links which involve the ring are not, in general, established during the polymerization.
- (8) Various unsaturated 5-membered ring structures are very prone to polymerize.
- (9) Cyclic olefines with six or more carbon atoms in the ring are comparable with corresponding open-chain olefines in their tendency to polymerize.*
- (10) The effectiveness of halogen substitution appears to be in the order I, Br, Cl.
- (11) Precise comparison of the polymerization tendencies of hydrocarbons is difficult on account of the catalytic effect of oxygen, and possibly other incidental catalysts, and also the effect of light.

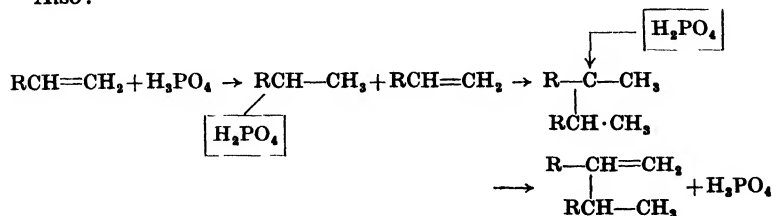
Varying pressures in the sealed tube in some cases reported in Tables I-V probably add uncertainty to the comparisons.

The mechanism of catalytic actions in polymerization is debatable (Table V). Aluminium halides are dominant; boron halides, especially BF_3 , which is less prone to give side reactions than AlCl_3 , with acids and halides, are preferentially used. Phosphorus oxy-acids and P_2O_5 are also used as polymerization catalysts. In olefine polymerization with H_3PO_4 , Ipatiev considers that the polymers are direct thermal decomposition products of the mono-alkyl esters of the acid. Whitmore⁸ suggests that the hydrogen of the acids adds to the double bond of the olefines, and that the complex behaves as a compound containing a carbon atom with only six electrons,



which is positively charged and can unite with a negative ion X or may unite with another olefine molecule.

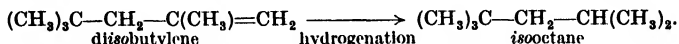
Also:



* The table from which conclusions Nos. 7, 8, and 9 are drawn is omitted.

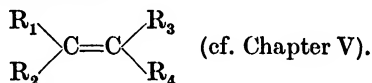
G. M. Kline and N. L. Drake¹⁰ suggest that C=C bonds are split with formation of corresponding free radicals in the acid catalysis of olefine polymerizations. The function of free radicals will be discussed shortly.

A reaction of far-reaching effect on the petroleum industry is the catalytic addition by H₂SO₄ of isobutane to isobutene to give 2, 2, 4-trimethyl pentane (isooctane) by hydrogenation (cf. p. 191).



Condensation polymerizations (cf. pp. 437-45) are no more mysterious than the individual steps of the reaction, which in some cases represent conventional reaction types, e.g. esterification. For such cases Flory¹¹ has derived expressions for distribution of polymer size as a function of the extent of reaction in those cases where linear polymers are expected. The only doubtful assumption he has made, according to Burk, is that the reaction rate of functional groups is independent of the size of the molecule to which they are attached. If this assumption be correct, reaction velocity does not enter further into the equations, although the ratio of the initial concentrations does.

Vinyl polymerizations:



Burk¹² summarizes the knowledge of the polymerization of vinyl hydrocarbons as follows:

(1) There is a difference between the polymerization in the vapour phase and the liquid phase, e.g. liquid styrene polymerizes, but styrene vapour is stable up to nearly the decomposition point. Harkness and collaborators¹³ could not induce vinyl acetate to polymerize in the vapour state below its decomposition point (420°), and they found that methyl-acetylene was stable up to 475°. Di-olefines will polymerize in the gas phase at atmospheric pressure, or below, in a temperature range of 285-435°; cyclopentadiene will polymerize in the gas phase at still lower temperatures. The difference between the gas and liquid phase behaviour has not yet been explained (cf. Melville, p. 431).

(2) The differences in polymerization rates of unsaturated compounds at low temperatures may be reduced or even reversed in order when the polymerization occurs in the vapour phase, e.g. 1, 3-butadiene polymerizes three times as fast as 2, 3-dimethyl-1, 3-butadiene at elevated temperatures, whereas Carothers¹⁴ reports that the latter compound polymerizes as fast as the former at lower temperatures.

(3) The influence of traces of oxygen and peroxides as catalysts is general for low-temperature thermal reactions. Active catalysts like

benzoyl peroxide and oxygen increase reaction velocity and reduce polymer mean size.

(4) Polyphenols (phenyl acetylene and benzoquinone in the case of styrene) act as inhibitors of polymerization; this is probably due to chain-breaking.

(5) Some vinyl polymerizations are inhibited by other unsaturated compounds present, a remarkable phenomenon from the point of view of the mechanism of the reaction. Paraformaldehyde reduces reaction velocity in the case of styrene and increases the mean mol. wt.

(6) Lower rates of polymerization give polymers of higher mol. wt. when the undiluted monomer is polymerized; this is in contrast to condensation polymerizations.

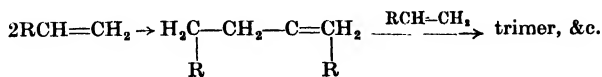
(7) The mol. wt. of high vinyl polymers is often more or less independent of the fraction polymerized under a given set of reaction conditions.

(8) There is a marked deficiency (deficiency here implies a comparison with probability expectations) of dimers and intermediate polymers in the products of vinyl polymerization in the liquid phase where high polymers are likewise formed. This is not necessarily true of dienes.

(9) Dimers, on the other hand, are the most prominent products in various gas-phase polymerizations. In the case of di-olefines these dimers are largely cyclic, and in the case of ethylene the low polymers are largely open chain, at least in the lower temperature ranges.

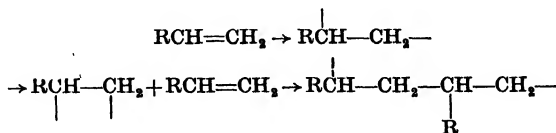
(10) Such vinyl polymerizations as have been investigated in the vapour phase appear to follow a bimolecular kinetic law. There are, however, certain incongruities upon which various authors place different weight, and which they interpret differently.¹⁵

(11) Some low-temperature polymerizations appear to follow a unimolecular law. Starkweather and Taylor report this behaviour for vinyl acetate. Schulz and Husemann¹⁶ report it also for styrene polymerization. The polymerization of $RCH=CH_2$ might be represented:

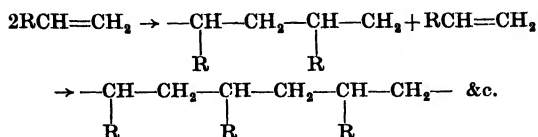


This stepwise type of reaction alone cannot account for all the above phenomena—in particular (1), (7), and (8).

Chain mechanisms. D. V. Sickman and O. K. Rice¹⁷ give the following representation:



This mechanism is considered by Burk to be doubtful energetically. Another representation is:



Such chain mechanisms have been discussed by W. Chalmers;¹⁸ Dostal and Mark ('Active nuclei');¹⁹ Dostal;²⁰ G. Gee²¹ (who speaks of activated molecules rather than free radicals); Gee and E. K. Rideal,²² who appear to assume thermal rather than material chains; G. V. Schulz,²³ who speaks of activated molecules rather than free radicals, and others.²⁴ The application of the free radical type of formation is shown in Table VI.

The influence of the solvent on the degree of polymerization has been observed by H. Staudinger and A. Schwalbach²⁵ in the diminution of the mol. wt. of vinyl acetate when polymerized in a benzene solution (1:1), in the presence of traces of acetaldehyde (Skirrow) and by Staudinger and E. Trommsdorff²⁶ in the polymerization of ethyl acrylate in butyl acetate solution, also by Staudinger in the polymerization of indene in benzene solution.²⁷ G. V. Schulz and E. Husemann²⁸ found that in the case of styrene the mean mol. wt. of the resulting polymer varied as the square root of the monomer concentration. According to these authors,²⁹ the kinetic results are explicable on the assumption that an endothermic intermediate is first formed between the styrene and the benzoyl peroxide, and this decomposes unimolecularly to an active form which serves as the starting-point or 'trigger'.

The coupling of free radicals with unsaturated molecules is usually associated with an activation energy of the order of 5,000 calories, so that the chain can continue (cf. p. 428). There are several theories for the cessation of polymeric growth:

- (a) collision of the free radicals;³¹
- (b) in the vinyl type the growing polymer is always an olefine, and the formation of a small ring at the end of the polymer is the cause of the cessation;³²
- (c) the steric factor in the velocity expression decreases progressively as the polymer grows.³³

It must be pointed out that there is in some cases evidence of the independent existence of bivalent radicals, and G. V. Schulz and G. Wittig³⁴ have shown that tetra-phenyl-succinonitrile dissociates into two free radicals, CPh_2CN , with styrene, and accelerates polymerization of the latter.

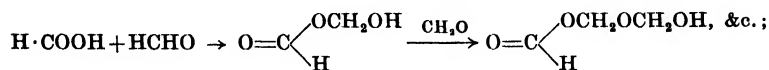
Catalytic chain mechanism. The 'stepwise' mechanisms for polymerization can be made to be consistent with the peculiarities of vinyl polymerization, if it be assumed that they are catalytic, when exhibiting chain characteristics, and that the catalyst remains

TABLE VI

Factors affecting Vinyl Polymerization

Chain initiation and induction period.	<p><i>Free radical mechanism</i></p> <p>(1) $\text{RCH}=\text{CH}_2 \rightarrow \text{R}\overset{\cdot}{\text{C}}\text{H}-\text{CH}_2\text{-}$</p>	<p><i>Catalytic mechanism</i></p> <p>(1) $\text{R}-\text{CH}=\text{CH}_2 + \text{Catalyst} \rightarrow \text{R}-\overset{\text{catalyst}}{\text{C}}\text{H}-\text{CH}_2\text{-}$</p> <p>(symbolic and does not imply a ring structure with the catalyst).</p>
Chain growth.	<p>(2) $\text{R}-\overset{\text{catalyst}}{\text{C}}\text{H}-\text{CH}_2\text{-} + \text{RCH}=\text{CH}_2 \rightarrow$</p> <p>(3) $\text{R}-\text{CH}_2-\overset{\text{catalyst}}{\text{C}}\text{H}-\text{CH}_2-\text{CH}_2-\text{R} \text{ &c.}$</p>	<p>(2) $\text{R}-\overset{\text{catalyst}}{\text{C}}\text{H}-\text{CH}_2\text{-} + \text{R}-\text{CH}=\text{CH}_2 \rightarrow$</p> <p>(3) $\text{R}-\text{CH}_2-\overset{\text{catalyst}}{\text{C}}\text{H}-\text{CH}_2-\text{CH}_2-\text{R} \text{ &c.}$</p>
Chain termination and chain transfer.	<p>(1) $\text{R}\overset{\text{R}}{\text{C}}\text{H}-\text{CH}_2(\text{RCH}-\text{CH}_2)_n-\overset{\text{R}}{\text{C}}\text{H}-\text{CH}_2\text{-} +$ $\text{R}_1\text{CH}=\text{CH}_2 \rightarrow \text{RCH}=\text{CH}-\overset{\text{R}}{\text{C}}\text{H}-\text{CH}_2\text{-}$</p> <p>$\text{R}\overset{\text{R}}{\text{C}}\text{H}-\text{CH}_2(\text{RCHCH}_2)_n-\overset{\text{R}}{\text{C}}\text{H}-\text{CH}_2\text{-}$</p>	<p>$\text{R}-\text{CH}_2\text{CH}_2(\text{RCH}(\text{CH}_2)_n-\overset{\text{catalyst}}{\text{C}}\text{H}-\text{CH}_2\text{-} +$ $\text{RCH}=\text{CH}_2 \rightarrow \text{RCH}-\overset{\text{catalyst}}{\text{C}}\text{H}_2\text{-} +$ $\text{R}-\text{CH}_2-\text{CH}_2(\text{CHCH}_2)_n-\overset{\text{R}}{\text{C}}=\text{CH}_2$</p> <p>Or catalyst-polymer complex dissociation.</p>
Temperature decreases chain length.	<p>Or recombination of radicals or increasingly important steric factors, &c.</p> <p>Chain transfer process for a higher temperature coefficient than chain growth.</p>	<p>Dissociation or transfer of catalyst from complex is facilitated.</p>
Dilution decreases chain length.	<p>$\text{R}-\overset{\text{R}}{\text{C}}\text{H}-\text{CH}_2(\text{RCHCH}_2)_n-\overset{\text{R}}{\text{C}}\text{H}-\text{CH}_2\text{-} +$ $\text{R}_1\text{CH}_2\text{R} \rightarrow \text{RCH}-\overset{\text{R}}{\text{C}}\text{H}(\text{RCH}:\text{CH}_2)_n-\text{CH}-\text{CH}_2-\text{R}_1$</p>	<p>Dissociation of catalyst from polymer is facilitated, preventing polymer growth.</p>
Mol. wt. of polymer sometimes independent of degree of polymerization.	<p>Chain-transfer mechanism has the same order as chain-propagating mechanism (Flory, <i>Amer. Chem. J.</i>, 1937, 39, 469).</p>	<p>Chain-transfer mechanism has same order as chain-propagating mechanism.</p>

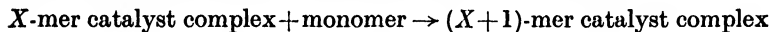
attached to the growing polymer. Examples of these mechanisms are supplied by (1) K. Ziegler³⁵ in the polymerization of 1, 3-butadiene with metallic sodium, and by the polymerization of 2, 3-dimethylbutadiene by lithium; (2) by J. M. Carruthers and R. G. Norrish³⁶ in the action of formic acid in the polymerization of formaldehyde



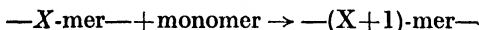
(3) by H. W. Melville³⁷ in the photo-polymerization of acetylene by mercury, whereby a metallic acetylene complex is formed and the growth of the polymer is stopped by a collision of another kind (e.g. a transfer collision).

In Table VI each element of free radical mechanism has its mathematical counterpoint in catalytic mechanism and none of the characteristics of vinyl polymerization is inconsistent with free radical polymerization.

The kinetic order of the chain initiation may be of first, second, or third classes, but it is thought by Flory³⁸ that the character of the conversion of the monomer to polymer is only slightly dependent upon the order of the interaction. Gee and Rideal³⁹ in a mathematical development of the catalytic complex theory obtained equations sufficiently flexible to account for all the experimental results. The kinetic constants which must be assigned to the scheme:



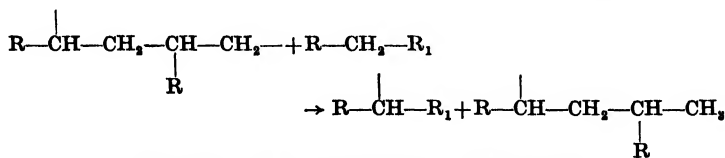
or



have not been determined directly, since more than one reaction has been involved.

The energy of activation of the possible bimolecular formation of free radicals has been estimated by Dostal and Mark⁴⁰ to be from 20,000 to 40,000 cal. per mol. and that for the chain-growth step from < 5,000 to 15,000 cal. The temperature-independent factors are known to be small for the initial step in the case of butadiene.⁴¹ The relative factors for chain initiation and chain-growth have been estimated by Mark and Raff⁴² on the basis of the theory of Dostal and Mark.

Burk concludes that definite knowledge of these factors is important as well as comparison with reactions of the type:

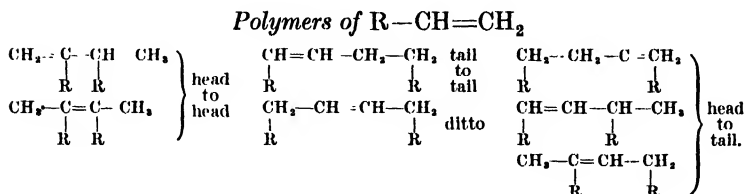


(where $\text{R}-\text{CH}_2-\text{R}_1$ is a solvent or a polymer).

Such reactions may prove to be a good criterion for appraising the free radical interpretation.

Burk's general conclusions as to the structure of polymers may be given:

- (1) Various configurations, head-to-head, head-to-tail, &c., have been reported in vinyl polymerization, but not necessarily more than one at a time under a given set of conditions:



- (2) It is not yet possible to predict the configuration of a polymer by any current theories.
- (3) Under some conditions of polymerization rearrangement of the product takes place; cf. E. H. Farmer and H. Brunner,⁴⁴ who found $\text{CH}(\text{CH}_3)_2-\text{CH}(\text{CH}_3)\cdot\text{CH}:\text{C}(\text{CH}_3)\cdot\text{C}(\text{CH}_3)_3$ to be formed by the action of BF_3 on tetramethylethylene at -10° to -60° .
- (4) There is no evidence that catalysts merely set off a free radical change mechanism which leads to the same polymer configuration independent of the catalyst used.

An excellent review of the progress of the investigations on polymerization problems is given by E. H. Farmer in the *Annual Reports* of the Chemical Society, 1936.

Polymers of lower olefines. The probable structures of polymers of the lower olefines is discussed fully by A. Wachter.⁴⁵ He states that there are two types of catalysed olefine polymerizations: (1) *Reaction proceeds at a comparatively slow rate and rarely goes beyond a C₁₆-C₂₀ product*; (2) *polymerization goes at a very high rate giving oily or resinous products*. The latter is probably polymerization with mechanism and kinetics very different from the first type.⁴⁶ The first type is dealt with by Wachter. He concludes that: (1) in the homologous series of olefine hydrocarbons the ease of polymerization increases from ethylene upwards and is at a maximum with the pentenes; (2) structural differences in isomers exert a marked influence upon the activity of the double bond.

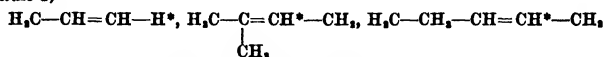
In general, tertiary olefines, e.g. 2-methyl-1-propene and 2-methyl-2-butene, are more readily polymerized than the corresponding isomeric secondary olefines, 2-butene and 2-pentene. The lower olefines may be arranged as follows: ethylene < propene < secondary butene < 2-methyl-propene; 2-methyl-1-propene; 2-methyl-1- and 2-butene > secondary pentenes > higher olefines.

(3) The di- and trimeric polymerization products of the lower olefines are far less easily polymerized than the monomer, e.g. 2-methyl-1-pentene is much more easily polymerized to octenes than

the latter to hexadecenes; moreover, the dimer is more readily polymerized than the trimer (Rule 1).

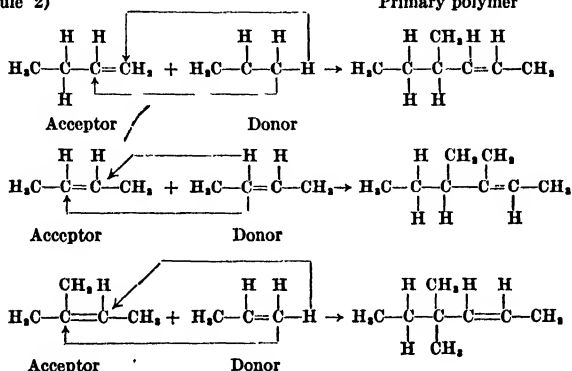
According to Wachter, there is an active hydrogen atom in the more negative of the doubly linked carbon atoms which is rendered active in the polymerization process: e.g.

(Rule 1)



* active hydrogen of the donor molecule.

(Rule 2)



Rule 2. In the 'acceptor' molecule one carbon atom with a double bond becomes attached to the active hydrogen atom from the 'donor', the other goes to the terminal double-bonded carbon atom, or to the one with the smallest alkyl group, and the olefine radical goes to the adjoining double-bonded carbon atom. When the 'acceptor' olefine contains a tertiary carbon atom with a double bond, the olefine radical from the donor always becomes attached to it, e.g. isopropylbenzene is the primary product of the reaction of propene with benzene.⁴⁷

Consideration of the rearrangement of the atoms in the molecule during polymerization is dealt with by two other rules, according to Wachter, founded on generalizations from the examination of a number of reacting systems, and the polymerization products of the lower olefines can be predicted by the rules formulated.

The rules of Wachter cannot have the general support given to the free radical hypothesis described by Burk. Nevertheless, they are founded on facts taken from the study of a great number of cases of polymerization of lower olefines. The rules may seem irrelevant to the study of resin foundation, but they illustrate the extensive research on the problems of polymerization of hydrocarbon systems proceeding at a slow rate and yielding substances of moderate complexity.

The formation of long-chain molecules has been reviewed by H. W. Melville.⁴⁸ In the case of styrene, methyl acrylate, and vinyl

acetate it has been established that the mechanism is of the chain type, in that when one molecule is brought into a reactive state by light or by a catalyst a large number of additional molecules may react with the active polymer more readily than they would with a normal molecule of the monomer.

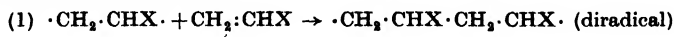
Kinetically, the problems to be solved are: How is the molecule brought into the reactive state? Is it possible for one molecule to possess more than one such state? When subsequent addition of monomer occurs, what is the efficiency of the process and how does it vary, if at all, with molecular size? Finally, by what type of reaction is the activity destroyed? Further problems of special interest are: Can branched reaction chains occur with the production of either branched or three-dimensional molecules? Is it practicable to cross polymerization chains, i.e. to form true inter-polymers? What is the distribution of the sizes of the molecules so produced?

In the study of gas-phase polymerizations only those mono-vinyl compounds containing the group $\text{CH}_2=\text{C}<$ interact, the exception being acetylene, which on irradiation with light of 2,000 Å. at 20° polymerizes to cuprene.⁴⁹ At higher temperatures isolable amounts of benzene are formed. Nothing is known of the constitution of cuprene, its mol.wt., or if it be a straight-chain compound. The photo-polymerization of methyl acetylene is rather less rapid than that of acetylene. Ethylene at 100–300°/ > 1,200 atmospheres forms a wax-like solid, and its polymerization in the presence of a controlled amount of oxygen is brought about under lower pressures by the free radical mechanism (cf. p. 428).⁵⁰

At high temperatures up to 300° methyl radicals from thermally decomposing azomethane,⁵¹ from photo-decomposing acetone,⁵² from thermally decomposing metal alkyls,⁵³ and ethyl radicals from photo-decomposing ethyl iodide⁵⁴ all polymerize ethylene to hydrocarbons up to C_{20} .

The free radical (CH_3) adds on to the ethylene molecule forming a larger free radical $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2$ —, whereby further molecules of ethylene are added on until the free radical reacts with another of its kind. The polymerization of hydrocarbons is not a reaction which occurs readily; if it be accelerated by employing higher temperatures the product is not stable. Fortunately, a number of vinyl derivatives have high enough vapour pressures to be studied in the vapour phase. In the case of methylacrylate⁵⁵ the polymer formed with ultra-violet light less than 2,600 Å. is reactive long after the light is cut off, and this activity is destroyed by atomic iodine, or atomic hydrogen, which are capable of reacting with double bonds or radicals.

The formation of the active vinyl polymer may be expressed by the following scheme:



or



In (2) there is a migration of a H atom each time a monomer is added,

and the double bond is excited so as to facilitate addition of a molecule of monomer, i.e. to reduce the energy of activation. The main characteristic of the chain mechanism is that once the first molecule is activated the activation energy for the subsequent addition is materially diminished.

This rearrangement of structure may be compared to Wachter's scheme (cf. p. 430).

Long-chain and dimer formation. In the liquid-phase polymerization of styrene both mechanisms may operate because a long-chain molecule or a di- or tri-styrene may be formed according to the conditions. Methyl acrylate presumably polymerizes by double-bond mechanism and chain termination is brought about by mutual destruction (cf. Chapter VI). The termination reaction possesses an energy of activation greater than that for propagation.

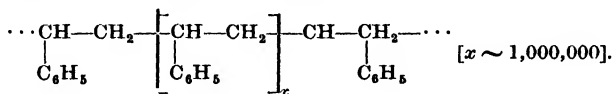
Chloroprene polymerized by irradiation shows two simultaneous reactions: one in which the life of the active molecules is short and polymerization is terminated by the interaction of two active ends of the molecule, and the other in which polymerization continues indefinitely. The energy of activation of polymer growth is about 3 kg.-cals. Since the lifetime of the methacrylate and chloroprene polymers is so long, it is possible to make mixed polymer methacrylate on chloroprene (co-polymer) and vice versa. On the other hand, butadiene refuses to inter- or co-polymerize with either of these molecules under these conditions. It has been pointed out earlier (p. 194), and may be stressed again, that the formation of interpolymers is of great practical importance. (Cf. polymerization of polyvinyl chloride and acetate and of butadiene with styrene and acrylic resins or olefines and diolefines in butyl rubber.)

Liquid-phase polymerization. More work has been done than in the gas phase, especially with vinyl acetate, methyl methacrylate, and styrene. In the presence of air, pure liquid styrene polymerizes at 100° as a homogeneous liquid-phase reaction. There is no induction period and the rate of reaction conforms to a first-order equation.⁵⁷ The average energy of activation is 23.2 kg.-cals. and the mol. wt. of the polymer decreases with increasing temperature according to the relationship $M = \text{const. } e^{5.700/RT}$. The mechanism of the cessation of growth involves the interaction of two active polymers.

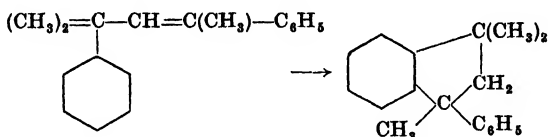
In a recent discussion on the polymerization of unsaturated hydrocarbons H. M. Stanley gives two essentially different types: (1) exclusively or mainly low polymers, e.g. dimerization of the lower olefines, whereby two monomer molecules unite and a hydrogen atom is transferred to the γ carbon atom of the dimer.⁵⁸ The theory of Whitmore (cf. p. 423) appears to agree with the observed facts.⁵⁹ The chain process is on the free radical hypothesis with an initial activation stage, in which activated molecules, possibly free radicals, are formed, and the chain termination is as previously described (cf. Table VI). In the influence of polymerization catalysts reference is made to the polymerization of the lower olefines to yield the so-called polymer gasoline under the influence of a phosphoric acid

catalyst (cf. p. 423). By effecting the polymerization of isobutene $\{(\text{CH}_3)_2\text{CH}=\text{CH}_2\}$ by BF_3 at low temperatures very high polymers are obtained of technical interest. Substitution of hydrogen by certain electro-negative groups, e.g. phenyl, CO, halogen, &c., increases the polymerization to high molecular weight polymers (cf. Tables III and IV).

The presence of one olefine bond in low mol.wt. polystyrenes, produced either thermally at elevated temperatures (250°) or at low temperatures in the presence of catalysts, has been established by measurements of their bromine numbers. The simultaneous existence of unsaturated low polymers of styrene with saturated polymers of the same molecular weight under the influence of catalysts has been confirmed by Stanley.⁶⁰ Commercial polystyrenes of mol.wt. 60,000–120,000 show the presence of one olefine bond. The general formula of polystyrene (cf. Chapter V) is given by Stanley⁶¹ as:



The conversion of the unsaturated dimer into a saturated dimer by catalysts can be illustrated in the case of methyl styrene:



Midgeley and collaborators support the formula:



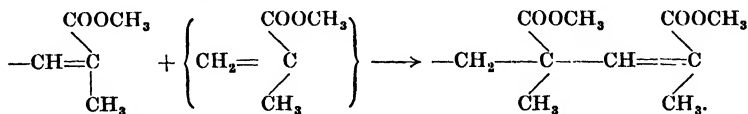
which they hold as being more consistent with the elastic properties of polystyrene.⁶² The thermal polymerization of styrene in solution has been discussed by A. Springer,⁶³ who refers to each of the polymerization stages: activation reaction, chain-growth, chain cessation in respect to styrene. Experiments at 80 – 140° on the polymerization of styrene in solvents, e.g. C_6H_6 , PhEt , CCl_4 , $\text{C}_2\text{H}_4\text{Cl}_2$, &c., show that the rate and degree increases with the solvents mentioned in the order given, and chlorine-containing polymerides are obtained illustrating the combination of the solvent (cf. Table VI).

The stabilizing action of quinol prevents the formation of styrene moloxide and so checks the catalysed initial reaction (see Table VI) and causes oxidation to quinone, which reacts with the growing nuclei and prevents chain formation.

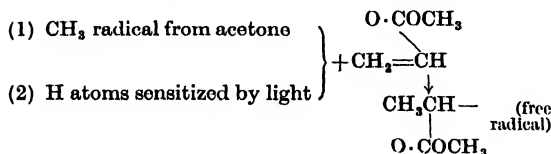
The production of co-polymers containing polystyrenes is of great interest (cf. Chapter V). Staudinger and Husemann⁶⁴ found that traces of divinyl benzene $\text{C}_6\text{H}_4(\text{CH}:\text{CH}_2)_2$ with styrene produced insoluble co-polymers, showing varying degrees of swelling in organic solvents (0.002 per cent. divinyl benzene had an appreciable effect).

The most recent contribution to the study of the mechanisms of polymerization is given by H. W. Melville, T. T. Jones, and R. F. Tuckett.⁶⁷ The formation of macromolecules from $\text{CH}_2=\text{CH}\cdot\text{Y}$ may be: (a) the monomer may be converted by the absorption of energy to give a diradical (cf. p. 431): to each end of this molecule monomeric molecules may be added, giving rise to a larger diradical e.g. free radical mechanism; (b) the monomer may be excited to an extent such that the addition of another monomer is facilitated (chain mechanism). In this mechanism there is always a terminal double bond in the macromolecule which is the centre of reactivity. It would appear possible to polymerize one and the same molecule by either (a) or (b), depending on the conditions. The difficulty is to decide which of (a) or (b) comes into operation. In the gas-phase polymerization it is often possible to settle the matter; e.g. H or CH_3 radicals add themselves on readily to vinyl derivatives, e.g. vinyl acetate, producing a single free radical with which the monomer easily reacts to form a linear polymer, until two such radicals combine to close the chain. By altering various parameters (according to Melville) it is easy to characterize this free radical growth and compare it with the polymerization under observation. If the kinetics be identical it must be supposed that the latter reaction is of the free radical type. In the *photo-polymerization* of gaseous vinyl acetate the kinetics are so different from those of the free radical reaction that it would seem as if the ordinary polymerization occurs by some double-bond mechanism. The difficulty yet to be solved is how the terminal double bond of the active molecule retains its activity. It is well known that a large number of molecules, including vinyl acetate, also polymerize in the liquid phase, and that a free radical polymerization has been induced in styrene,⁶⁸ by the addition of tetraphenyl succinonitrile, which dissociates to free radicals, CPh_2CN , in solution (cf. p. 426).

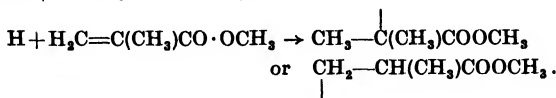
In the direct photo-polymerization of vinyl compounds the active polymer is *not* a free radical, and it has been suggested that migration of a hydrogen atom is involved when the monomer acts on the active polymer: e.g.



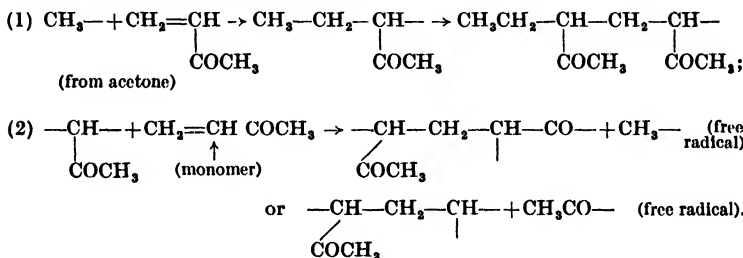
In the radical sensitized reactions by means of acetone or hydrogen, with illumination of 3,000 Å., the scheme is stated to be:—



In the case of methyl methacrylate the scheme would be:



In the case of vinyl-methyl-ketone ($\text{CH}_2=\text{CH}\cdot\text{COCH}_3$) and isopropenyl-methyl-ketone ($\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}\cdot\text{CH}_3$) on polymerization with an illumination of 3,000 Å., the former ketone acting more readily than the latter (methyl-substituted vinyl derivatives are more difficult to polymerize than the parent molecules, see Table II), the vinyl-methyl-ketone (gaseous) is decomposed, and it may be that among the products of decomposition are free radicals whereby polymerization may be induced. This was shown by Melville to be the case, but the product of the reaction is insoluble in solvents, which points to cross-linkage, and the kinetics of the reaction can be explained by branching of the growing molecules. The action of decomposition products of acetone with vinyl-methyl-ketone as well as the branching when a polymer-free radical collides with a monomer, may be illustrated by the schemes:



A. C. Cuthbertson, G. Gee, and E. K. Rideal⁶⁹ state that the polymerization of vinyl acetate is homogeneous and is catalysed by benzoyl peroxide. The catalyst reacts with the monomer to form a complex (see Table VI), which on breaking down initiates a polymer chain. Kinetic analysis shows that the termination is again due to mutual interaction of active polymers. Further complication appears to arise, for at high temperatures the polymer becomes insoluble, from which it is concluded that branching and cross-linking of the molecular chain occurs. The kinetics of the polymerization of methyl methacrylate (catalysed by its ozonide and by benzoyl peroxide) has been studied by R. G. Norrish and E. F. Brookman.⁷⁰ The rate of polymerization is proportional to the square root of the catalyst concentration, which implies mutual destruction of the active polymers, whatever these molecules may be (cf. Chapter VI). Melville in conclusion of his paper states that the kinetic attack on the problem, supplemented by the determination of the structure of the resultant polymer, does show some promise of obtaining successful solutions of problems.

The primary investigations of the polymerization of hydrocarbons,

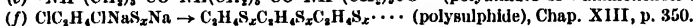
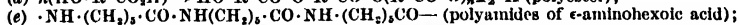
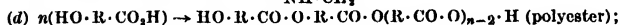
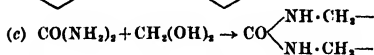
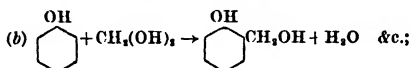
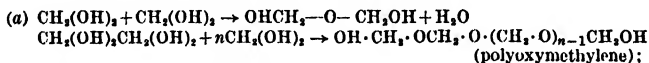
which have been stated in considerable detail, together with the theories arising from such investigations, have been continued by examination of systems, e.g. styrene, vinyl acetate, and methyl methacrylate, so that an approach has been made to problems arising from the study of technical resins, and Melville's conclusions are of great value.

The results are applicable to the thermoplastic resins, where cross-linkages between the chains do not occur.

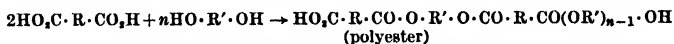
The introduction of cross-linkages in the polymerization of styrene by traces of divinyl benzene to give a thermo-setting polymer further links up the connexion with industrial plastics (cf. Chapter V).

MULTI-CONDENSATIONS (CONDENSATION POLYMERIZATIONS)

This class of polymers (*C* polymers of Carothers) has received more attention from a technical standpoint than the straight-chain and cross-linked polymer formed by interaction of functionalities as in the hydrocarbons, vinyl, and methacryl derivatives. The polyoxymethylenes of Staudinger (*a*), the bakelites of Baekeland (*b*), the urea-formaldehydes (*c*), the alkyds (*d*), polyamides, and polysulphide resins (*e*) are in their early stages formed by the elimination of water or HCl from the interacting components, e.g.:



It is to class (*d*) of polymers that Kienle has applied his postulates (cf. p. 442) generalizing on the conclusions drawn by Carothers on the interaction of dibasic acids and glycol (polyesterification):



(R, R' = bivalent groups, e.g. polymethylene).

The work of Carothers and Arvin⁷¹ and with G. L. Dorrough⁷² on the condensation of dibasic acids with glycols has produced products which are partly crystalline and partly vitreous solids. In molten condition they are very viscous and are generally soluble in solvents unless the polymerization has been carried too far. The molecular weights vary between 2,500 and 3,000. When prepared at lower temperatures products are obtained which are viscous fluids, passing on further condensation to hard substances. These preparations are not simple substances but are mixtures of chains, similar, and of different lengths. Some of them show crystalline properties and

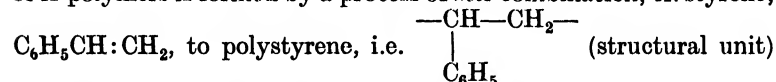
resemble mesophases (a mesophase is a transitional form between the fluid and crystalline condition) of the type:



in which x and y must be greater than 2. Well defined crystals are not obtainable, but are of the form of doubly refracting microscopic spherulites, which group together in a star-like pattern.

From the work of H. Zecher⁷³ it may be concluded that the long string molecules lie against one another and produce anisotropic crystal-like patterns without forming regular crystals. A similar appearance is noticed in crystalline paraffin mixtures (hard and soft paraffins), and is favoured by the symmetrical structure of the main valence chain as in the above formulae. The microphotogram of trimethyl cellulose resembles that of ethylene succinate, and the crystalline character may be connected with the occurrence of mixtures of molecules whose lengths are 50–150 Å. and favour a bundle-like arrangement (cf. pp. 505–9). It must be borne in mind that the physical characters of some colloids of the same formula may be different owing to a *cis-trans* configuration of the chain.⁷⁴

It is advisable to quote fully from the papers by Carothers and his collaborators, which cover a wide field of investigation up to the date of his death. In the conclusion of one of his earlier papers in 1929 Carothers⁷⁵ states that the process of polyintermolecular condensation finds no mention in treatises on polymerization. The addition of A polymers is formed by a process of self-combination, cf. styrene,



(cf. Chap. V, p. 192). The polymeric molecule is generally heat-convertible into a monomer. Chemists have in consequence assumed that condensation leads directly to the formation of small molecules, and, if large molecules be formed, this is due to the intervention of unsaturated molecules capable of undergoing A polymerization.⁷⁶ It is quite certain, however, that in cases of condensation polymerization no such intermediate products occur. The C (condensation) polymers are converted by hydrolysis or its equivalent to a monomer, which differs in composition from the structural unit by one H_2O (or HCl , NH_3 , &c.), or the polymeric molecule is formed from numbers of monomers by a process of polyintermolecular condensation. Rubber, polystyrene, polyoxymethylenes, and para-acetaldehyde are A polymers. Cellulose, silk fibroin, and polyethylene glycols are probably C polymers. The mere assumption that unsaturated intermediates intervene in a reaction which leads to high polymers of the A class contributes little to the knowledge of the mechanism of the process or of the structure of the product. The essential peculiarity of polymerizations is that they are intermolecular combinations functionally capable of leading to molecules of infinite size (Carothers).

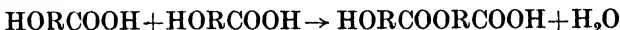
C polymerization involves the use in multiple fashion of common

functional groups. Substances of the type $x-R-x$ and $x-R-y$ are called bifunctional (Carothers). In these formulae $-R-$ represents a bivalent radical and x, y are functional groups, capable of reacting with each other in a known fashion to form a new functional group z . Among bifunctional compounds these reactions may proceed in such a way as to guarantee the structure of the unit $-R-z$, in the polymer $(-R-z-)$ formed.

Reactions of the type $x-R-y \rightarrow$ product are called bifunctional and reactions of the type $x-R-x + y-R-y \rightarrow$ products are called bi-bifunctional; such reactions will lead to compounds containing the structural units $-R-z$ and $-z-R-z-R$ respectively. The compounds formally capable of polymerization are polyfunctional. A double bond or reactive ring will count as a double function.

In the investigation of the esters of dibasic acids and dihydric alcohols (a bifunctional reaction) Carothers and Arvin⁷⁷ stated that the esters will polymerize unless the number of atoms in the chain of the structural units is less than 7. The molecular weight of the chain substance from ethylene malonate was found to be 2,500-3,500. The polymerism of the glycol esters of dibasic acids is a polymerization of intermolecular condensation and not the addition of monomeric species. When, in the interaction of a dibasic acid with a dihydric alcohol, the number in the chain of the structural unit $-R-$ is too great to permit a 5- or 6-member ring formation, then the reaction becomes polymolecular and the polymers are linear in type, $-(-CO-(CH_2)_x-CO-O-(CH_2)_y-O-)-$. Bifunctional reactions can yield only linear polymers, and solubility and fusibility are not lost even at very high molecular weights. If glycerol be used the products may be insoluble and infusible because of 3-dimensional spatial arrangement.

The term 'polyfunctional' requires further consideration.⁷⁸ In the reaction



the first product is a dimer containing two structural units. Half the initial functional groups have disappeared; similarly, it is evident that the formation of a trimer will involve 67 per cent. reaction and a tetramer will correspond to 75 per cent. reaction. In general, if p is the degree (function) of the reaction and x is the average degree of polymerization,

$$p = 1 - \frac{1}{x}; \quad (1)$$

e.g.

$$\begin{array}{l} p = 0; 0.5; 0.8; 0.9; 0.95; 0.99; 0.999 \\ x = 1; 2; 5; 10; 20; 100; 1,000 \end{array}$$

The general equation developing degree of reaction polymerization and functionality can be developed as follows:

Let f = degree of functionality (number of functional groups per monomer molecule).

N_0 = number of monomer molecules initially present.

Then N_0f = number of functions initially present.

N = number of molecules after the reaction has occurred.

$2(N_0 - N)$ = number of functions lost.

$\frac{2(N_0 - N)}{N_0f}$ = fraction of functions lost = p = (extent of reaction).

$\frac{N_0}{N}$ = average degree of polymerization = x .

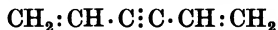
Hence $\frac{2}{f} - \frac{2}{xf} = p$ = degree of reaction. (2)

If x be very large, then $p = 2/f$, which tells at what degree of reaction the molecular weight is infinite, or where in polyfunctional reactions gelations will occur and intermolecular reaction cease.

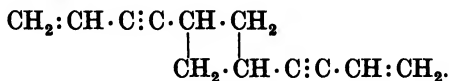
For a bifunctional reaction $p = \frac{2}{f} = 1$, and since this value can never be reached actually, gelation will not occur.

For a trifunctional reaction the limit will be at $p = \frac{2}{3}$, for a tetra-functional reaction at $\frac{1}{2}$; for this reaction at $x = 100$, $p = 49.5\%$: thus the average molecular weight will suddenly change from a moderate to a colossal value with very little change in the extent of reaction.

In attempting to apply formula (2) the chemistry of the system must be taken into account. A double bond will count as a double function only if the reaction be exclusively intermolecular at every stage. Multiple-function compounds often do not exercise all their functions together. In the formation of polyprenes from dienes only the 1, 4 positions of the latter are first called into play. The remaining double bond of each unit functions under slightly different conditions to cause cross-linking. Acetylene would be a tetrafunctional compound and probably behave as such in the formation of cuprene (p. 431). In the formation of divinyl acetylene,



(p. 434), only half of its unsaturation is involved, and it behaves in the early stages of its thermal polymerization like a bifunctional compound, yielding



Perhaps a majority of the reactions to which equation (2) would be applied are of the AB type involving two reactants of complementary function. If each reactant be bifunctional, A^2B^2 , the reaction as a whole will be bifunctional: if A^3B^3 , is trifunctional, &c. If A and B have different number of equivalents per molecule the situation is more complicated, e.g.:

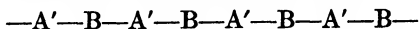
(a) In the reaction between glycerol and phthalic anhydride (A^3B^2) there are 2 mols. of glycerol and 3 of phthalic anhydride, or 5 in all,

containing 12 equivalents; and then $f = \frac{12}{5} = 2.4$. Then at $x = \infty$,

$p = \frac{2}{2.4}$, and the limit of the reaction will be $\frac{5}{8}$ (83.3 per cent.).

This represents the maximum amount of reaction that can occur before gelation, provided that the reaction is intermolecular.⁶²

(b) Another possibility is the following: if glycerol behaves at first as though it were bifunctional, yielding a chain



(' indicates unreacted hydroxyl) then all the molecules of glycerol could be combined into one with the loss of only $\frac{2}{3}$ of the functional groups ($\frac{1}{3}$ of the phthalic anhydride remains entirely unreacted). Here $f = 3$ and 66.7 per cent. is the minimum extent of the reaction compatible with gelation. Experimental values found by various investigators generally lie between 75 and 80 per cent. (cf. Chap. XI, p. 281).

	Structural unit $-R-$	Mol. wt.	m.p.	
Ethylene malonate		2,300-3,500	liquid	
Ethylene succinate		2,300-900	108°	
Ethylene adipate		2,998	50°	
Trimethylene succinate		3,500-4,300	52°	
Trimethylene adipate		2,400-4,300	45°	
Hexamethylene succinate		3,200-500	57°	
Decamethylene sebacate		3,100	74°	
Ethylene carbonate		76-73	b.p. 238°	Number of atoms in structural unit 5
Trimethylene carbonate		105,104	m.p. 47-48°	
Polymeric		3,880-4,670	A glass, changing to a powder m.p. 59	6
Tetramethylene carbonate		1,290-450		
Hexamethylene carbonate		2,610-970	honey-like and elastic	9
p-Xylylene carbonate (soluble)		810-40	powder m.p. 137	9
p-Xylylene carbonate (insoluble)		1,010-30	powder m.p. 177	9

The ethylene, trimethylene, hexamethylene, and decamethylene esters of malonic, adipic, and sebacic acids have been obtained as crystalline compounds and all are polymerized (see table, p. 441); the structural unit ranges from 7 to 22 atoms, and the molecular weight from 2,300 (ethylene malonate) to 5,000 (trimethylene sebacate). Ethylene and trimethylene carbonates are obtainable, as would be expected, in the monomeric form, but the latter can be converted on heating with potassium carbonate into a true polymeride, from which the monomeric ester is regenerated on distillation *in vacuo*.

Neutral and acidic ethylene succinates, showing different degrees of polymerization, have been prepared and mixed polymerides have been obtained by the interaction of ethylene glycol with equivalent quantities of succinic and sebacic acids, but not by fusing polymerized ethylene succinate and ethyl sebacate. Chemical and osmotic methods have given concordant results for the molecular weights of these substances.⁷⁹

KIENLE'S POSTULATES

The importance from a practical point of view of the changes which occur when dibasic acids (anhydrides) are esterified with trihydric alcohols is greater than the interaction of such anhydrides with dihydric alcohol. R. H. Kienle⁸⁰ has discussed gelation phenomena of synthetic resins and other organic polymers. He points out that the industrial usefulness of synthetic resins and other organic polymers depends largely on their ability to be transformed into a so-called insoluble infusible type. This conversion process is generally referred to as polymerization, although, strictly speaking, it is a sol-gel transformation and may be differentiated from the evaporation of a synthetic resin in a solvent to form a film. Three classes of organic polymers are obtainable depending on their ability to gelate or upon their mechanism of gelation, viz. heat-convertible (polyolefines, glyptals, bakelite C (alkaline)), heat-non-convertible (cf. novolaks (acid) and styrene), and element-convertible (drying-oils).⁸¹ Synthetic polymers of all these classes have been prepared, the fundamental reaction of preparation being either condensation, addition, or both. In the glyptals convertible, non-convertible, and element-convertible types have been prepared together with amorphous powders and crystalline compounds on the same basic chemical reaction, viz. condensation of a hydroxyl group and a carboxyl group. These studies have provided a formulation of three postulates of resin formation.

Postulate No. 1. Organic compounds of high molecular weight are formed only when the interacting molecules are polyreactive, i.e. possess the capability of uniting with one another through more than one primary valence bond. No high polymer is formed unless the reaction activity is 2, 2 (styrene is 2, 2 activity). (It must be remembered, however, that Meyer and Mark (loc. cit.) stress the importance of considering secondary valency forces, e.g. association,

and assume that secondary valency forces act between chain molecules forming micelles. Reference will be made later to the works of others in this direction.)

Postulate No. 2. Interlinking of molecules proceeds according to the chance contact of any two individual reactive points (random bonding of polyreactive molecules is responsible for heterogeneity, polymeric complexity, and the colloid properties of high polymers).

Postulate No. 3. The relative size and shape of the reacting molecules and the position of the reactive points largely determine the physical properties of the resulting products (e.g. hardness, flexibility, heat-convertibility).

The reactivity of a few substances may be given to explain the figures 2, 2 and 2, 3, &c. Styrene polymerization is 2, 2; coumarone polymerization is 2, 2. Glycol-ester condensation with a dibasic acid is 2, 2, whilst glycerol with a dibasic acid is 2, 3; linoleic acid polymerization is 4, whereas condensation has a reactivity of 2; formaldehyde condensation has a reactivity 2, phenol also 2, and urea 2, 4. A general survey of synthetic resins and other high polymerides by Kienle is given below.

Kienle states that he has been able to predict the properties of condensation and polymerization products by applying the above postulates. There would seem to be a difficulty in the rather speculative character of the reactivities of various substances, e.g. the phenol-aldehyde reaction (acid) is a 2, 2 reaction, but 4, 2 for alkaline reaction. In his prediction of physical properties he concludes that if the distance between reactive groups in one of the reactive molecules in a polymer be increased, a softer and more fusible product will result, e.g.:

Phthalic anhydride (2), and methyl alcohol (1)	give no resin.
„ and ethylene glycol (2)	give a hard glossy resin.
„ „ propylene glycol (2)	„ hard resin.
„ „ diethylene glycol (2)	„ balsam.
„ „ glycerol (3)	„ hard glassy resin.
„ „ mannitol (6)	„ hard opaque resin.

(The figures denote the respective reactivities.)

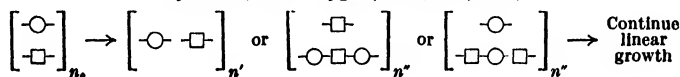
If the number of reactive bonds per molecule were increased, the separate parts of the polymeric molecule would be more rigidly and compactly held in position and there would be an increase in the fluidity-point on melting.

With reference to element-convertible polymers of drying-oils with the di-reactivity of oxygen and poly-reactivity of the oils the principal reactivity is aggregation of oil molecules through the agency of oxygen linkages. This view seems to be correct (R.S.M.), although the position of the oxygen molecules is a dominant factor in the polymerization, and not all the unsaturated double linkages, although oxidized, are polymerizable, e.g. β -eleaostearic and maleic anhydride adduct gives a polymerizable peroxide, but not the α -eleaostearic acid compound.

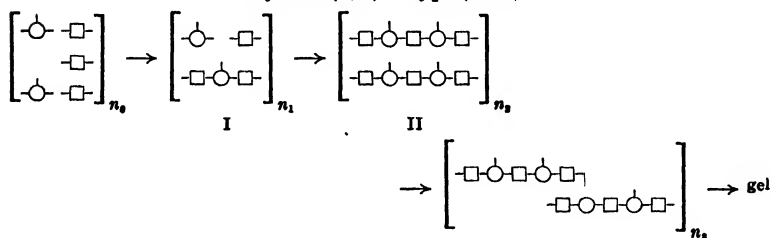
In a paper on the structural chemistry of synthetic polymers

Kienle³² gives an excellent review of the recent progress in that field, quoting most of the authorities already referred to in this chapter. He proposes to change Postulate 2 to read: (1) the interlinking of the molecules proceeds according to the chance interaction of any two individual reactive points which possess the proper degree of activation to bring about interaction; (2) to differentiate between potentially functional and actively functional groups, radicals, and atoms, they being only actively functional when they are acting intermolecularly; (3) to suggest that in a system involving the interaction of polyfunctional molecules, the progress of polymeride formation is such that as each intermediate product or polymeric molecule is formed, the *functionality of that intermediate product or polymeric molecule shall be considered, as far as further reaction is concerned, as if the newly formed molecule were a monomeric* (this modification arises from inability of drawing definite conclusions as to when gelation will occur in polymeric systems higher than those of the (2, 2) type according to Carothers' degree of functionality (p. 438): functionality rather than the number of molecules determines the degree of polymerization). In the following scheme this view is illustrated.

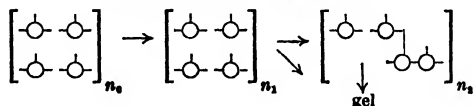
System (2, 2). Type (A, A) or (A, B)



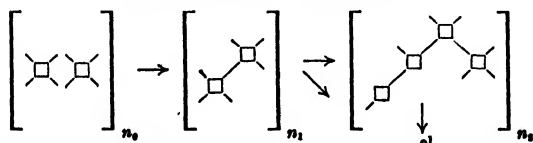
System (2, 3). Type (A, B)



System (3, 3). Type (A, A)



System (4, 4). Type (A, A)



Postulated progress of polymeric systems (Kienle)

In considering the revised polymeric theory in its entirety, when the reaction reactivity is $(1, N)$, where N can be any integer, a pure compound results, except where steric hindrance or presence of isomerides lowers the effectiveness of the vector forces of crystallization, in which case, if a solid forms it will be crystalline. When the functionality is 2 a linear non-convertible polymeride will result. Whenever reaction reactivity is (N, M) , and N is any integer 2 or greater, M any integer 3 or greater, a convertible polymeride is formed.

Kienle is optimistic towards the approach to a clearer and closer satisfactory understanding of the structure of synthetic polymerides. He advocates the share of all branches of science in the complicated field and points out that some semblance of order is being evolved out of such a chaos of organic products. In the opinion of the writer of this chapter the recent change in the postulates is of interest as indicating the elasticity necessary for a closer connexion between theory and practice.

REFERENCES

1. *Chem. and Ind.*, 1940, 59, 434.
2. *Trans. Faraday Soc.*, 1935, 31, 48.
3. *Nature*, 1938, 142, 937.
4. *Loc. cit.*
5. *Ind. Eng. Chem.*, 1938, 30, 1054.
6. W. H. Carothers, *Trans. Faraday Soc.*, 1936, 32, 39.
7. *J. Amer. Chem. Soc.*, 1937, 59, 466.
8. *Ind. Eng. Chem.*, 1934, 26, 94.
9. L. A. Monroe and E. R. Gilliland, *Ind. Eng. Chem.*, 1938, 30, 58.
10. G. M. Kline and N. L. Drake, *Nat. Bur. Standards J. Research*, 1934, 13, 705.
11. *J. Amer. Chem. Soc.*, 1936, 58, 1877; 1937, 59, 460; 1940, 62, 1561.
12. *Loc. cit.*
13. J. B. Harkness, G. B. Kistiakowsky and W. H. Mears, *J. Chem. Phys.*, 1937, 5, 682.
14. *Ind. Eng. Chem.*, 1938, 30, 1058.
15. A. Wassermann, *J.C.S.*, 1936, 1028.
16. *Z. physikal. Chem.*, 1937, B 36, 184.
17. *J. Chem. Phys.*, 1936, 4, 608.
18. *J. Amer. Chem. Soc.*, 1934, 56, 912.
19. *Z. physikal. Chem.*, 1935, B 29, 290; *Z. angew. Chem.*, 1937, 50, 348.
20. *Monatsh.*, 1935, 67, 163; 1936, 69, 424; 1937, 70, 409.
21. *Trans. Faraday Soc.*, 1936, 32, 656.
22. *Ibid.*, 1936, 31, 960.
23. *Z. physikal. Chem.* 1935, B 30, 379.
24. G. V. Schulz and E. Husemann, *ibid.*, 1936, B 34, 187; P. J. Flory, *Amer. Chem. J.*, 1937, 59, 204; H. Dostal, H. Mark, and R. Raff, *Ind. Eng. Chem.*, 1937, 29, 595; H. Mark, *Chem. Weekblad*, 1935, 33, 514; N. N. Semenov, *Uspekhi Khim.*, 1936, 3, 321; C. E. H. Bawn, *Trans. Faraday Soc.*, 1936, 32, 178.
25. *Annalen*, 1931, 488, 39, and F. W. Skirrow, *Chem. Ind.*, 1938, 1117.
26. *Ibid.*, 1933, 502, 208.
27. *Helv. Chim. Acta*, 1929, 12, 935.
28. *Z. physikal. Chem.*, 1937, B 36, 194; 1938, B 39, 246.
29. J. W. Breitenbach, A. Springer, and E. Abrahamczik, *Östen. Chem. Ztg.*, 1938, 41, 182; A., 1938, 268.
30. J. W. Breitenbach and A. Springer, *Ber.*, 1938, B 71, 1438.
31. G. V. Schulz and E. Husemann, *Z. physikal. Chem.*, 1935, B 30, 379.
32. J. Risi and D. Gauvin, *Can. J. Research*, 1936, B 14, 255.
33. G. Gee and E. K. Rideal, *Trans. Faraday Soc.*, 1936, 32, 656.
34. *Naturwiss.*, 1939, 27, 387.
35. *Z. angew. Chem.*, 1936, 49, 499.
36. *Trans. Faraday Soc.*, 1936, 32, 195.
37. *Ibid.*, 1936, 32, 628.
38. *J. Amer. Chem. Soc.*, 1937, 59, 469.
39. *Trans. Faraday Soc.*, 1935, 31, 969.
40. *Z. angew. Chem.*, 1937, 50, 348; *Z. physikal. Chem.*, 1935, B 29, 290.
41. J. B. Harkness, G. B. Kistiakowsky and W. H. Mears, *J. Chem. Phys.*, 1937, 5, 682.
42. *Z. physikal. Chem.*, 1936, B 31, 275.
43. R. E. Burk, *loc. cit.*
44. *J.C.S.*, 1937, 1039.

45. *Ind. Eng. Chem.*, 1938, 30, 822.
46. H. Carothers, *Chem. Rev.*, 1931, 8, 2390.
47. J. F. McKenna and F. J. Sowa, *J. Amer. Chem. Soc.*, 1937, 59, 470.
48. *Ann. Reports Chem. Soc.*, 1939, 67.
49. S. C. Lind and R. S. Livingston, *Amer. Chem. J.*, 1932, 54, 103.
50. B.P., 71,590; B., 1937, 1309.
51. O. K. Rice and D. V. Sickman, *J. Amer. Chem. Soc.*, 1935, 57, 1438.
52. J. C. Jungers and H. S. Taylor, *J. Chem. Phys.*, 1935, 3, 338.
53. H. S. Taylor and W. H. Jones, *J. Amer. Chem. Soc.*, 1930, 52, 1111.
54. G. Joris and J. C. Jungers, *Bull. Soc. Chim. Belg.*, 1938, 47, 135.
55. H. W. Melville, *Proc. Roy. Soc.*, 1937, A 163, 511.
56. J. W. Breitenbach and W. Jorde, *Z. Elektrochem.*, 1937, 43, 609; H. Dostal and W. Jorde, *Z. physikal. Chem.*, 1937, 179, 23.
57. G. V. Schulz and E. Husemann, *ibid.*, 1938, B 39, 246.
58. *Chem. Ind.*, 1939, 1080.
59. *Ind. Eng. Chem.*, 1934, 26, 94.
60. J. Risi and D. Gauvin, *Can. J. Research*, 1936, 14 B, 255.
61. *Chem. Ind.*, 1938, 141.
62. *J. Amer. Chem. Soc.*, 1936, 58, 1961.
63. *Kautschuk*, 1938, 139, 197, 201, 212; B., 1939, 172.
64. *Ber.*, 1935, 68, B 1618.
65. *Proc. Roy. Soc.*, 1937, A, 163, 205.
66. *J. O. C. Chem. Assoc.*, 1939, 22, 201.
67. *Chem. Ind.*, 1940, 59, 267; *Nature*, 1940, 145, 248.
68. G. V. Schulz and G. Wittig, *Naturwiss.*, 1939, 27, 387.
69. *Proc. Roy. Soc.*, 1939, A, 170, 300.
70. *ibid.*, 147.
71. *J. Amer. Chem. Soc.*, 1929, 51, 2560.
72. *ibid.*, 1930, 52, 711.
73. *Physikal. Z.*, 1927, 28, 790.
74. K. H. Meyer and H. Mark, *loc. cit.*, pp. 62 and 105.
75. *J. Amer. Chem. Soc.*, 1929, 51, 2548; 1932, 54, 1579.
76. A. A. Drummond, *Trans. Inst. Rubber Ind.*, 1928, 4, 40 and J. Scheiber, *Chem. Umschau*, 1928, 15, 181.
77. *J. Amer. Chem. Soc.*, 1929, 51, 2560
78. Carothers, *Trans. Faraday Soc.*, 1936, 32, 43.
79. Carothers, *J. Amer. Chem. Soc.*, 1930, 52, 314, 711, 3292, 4110.
80. *Trans. Faraday Soc.*, 1935, 31, 48.
81. B. H. Kienle and J. W. Ferguson, *Ind. Eng. Chem.*, 1929, 21, 349; 1930, 22, 500.
82. *J.S.C.I.* 1936, 55, 229 r.


CHAPTER XVI

THE PROBLEMS OF RESINIFICATION. II

IN the previous chapter the characteristics of polymerization and condensation polymerization were discussed, and it is advisable to consider in detail the properties of a number of resinous and plastic materials before proceeding to communicate the general conclusions drawn by the many investigators in this field. Only a few classes will be referred to as the properties of the majority have been dealt with in earlier chapters.

POLYOXYMETHYLENES

The pioneer work of Staudinger on the polyoxymethylenes must be described in general, in view of the subsequent development of the other types of multi-condensations referred to above although the results are of no important direct technical application. The functions of formaldehyde in Bakelite resins have been discussed in Chapter III.

	<i>Monomeric</i>	<i>Polymeric</i>
Polyoxymethylene	$H_2C:O$	$\dots CH_2[OCH_2]_n OCH_2 O \dots$
Polystyrol	$C_6H_5CH:CH_2$	$\dots CH_2[CH \cdot C_6H_4CH_2]_n CHC_6H_5 \dots$
Polyacrylic acids	$CH_2:CH \cdot COOH$	$\dots CH_2[CH(COOH) \cdot CH_2]_n CH \cdot COOH \dots$
Polyethylene oxide	CH_2-CH_2 	$\dots OCH_2 \cdot CH_2[OCH_2 \cdot CH_2]_n \cdot O \dots$
Polyvinyl acetate	$CH_2:CH \cdot O \cdot CO \cdot CH_3$	$\dots CH(O \cdot CO \cdot CH_3) \cdot [CH_2 \cdot CH(OCOCH_3)]_n CH_2 \dots$
Polyvinyl bromide	$CH:CHBr$	$\dots CH_2[CHBr \cdot CH_2]_n CH \cdot Br$
Polyallyl chloride	$CH_2:CH \cdot CH_2Cl$	$\dots CH(CH_2Cl)CH_2:CH(CH_2Cl)]_n CH_2 \dots$
Polyanethol	$CH(C_6H_5OCH_2):CHCH_2$	$\dots CHR[CH(C_6H_5OCH_2) \cdot CH(CH_2)]_n CHR \dots$
Polyindene	$C_6H_4-\overset{..}{CH}$ CH_2-CH	$\begin{array}{c} -CH-CH- \\ \quad \\ C_6H_4-CH_2 \quad [C_6H_4-CH_2]_n -CH \dots \end{array}$

It is evident that as the chain lengthens the percentage of the active terminal components becomes smaller and smaller, so that their reactivity is at first sight (cf. p. 440) a measure of the length of the chain; cf. the estimation of the acetyl content in polyoxymethylene diacetates, which Staudinger obtained by the splitting of different modifications of paraformaldehyde with acetic anhydride, whereby a mixture of polymethylene diacetates was produced containing 2-20 formaldehyde groups which have united to form a molecule:

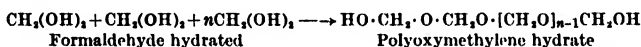


The lower compounds up to 20 formaldehyde groups may be

separated by fractional crystallization and characterized as uniform substances.

Formaldehyde content	Mol. wt.	Boiling-point	Melting-point	Solubility
1	132	164-165°	..	miscible with ether
4	222	132-144° (2 mm.)	..	miscible with ether
7	312	180-190° (0.3 mm.)	about 15°	very soluble in ether
8	342	decomposes	27.5-28.5°	very soluble in ether
12	462	„	66-67°	slightly soluble in ether
20	702	„	above 120°	insoluble in ether

In addition to the above polyoxymethylene diacetates, insoluble substances with small acetyl values containing at least 30 formaldehyde groups were obtained. These crystal-like substances are probably a mixture of polymerization products, i.e. thread-like molecules of main-valency chains of different lengths, so that the molecular weights represent only an average value. Staudinger and his collaborators have described other series of polyoxymethylenes, which differ not only in the average length of the chain, but also in the character of the end groupings.



	<i>Behaviour in sodium sulphite solution</i>
α -polyoxymethylene HO—CH ₂ —O—...—O·CH ₂ OH—a hydrate	soluble
β -polyoxymethylene HSO ₃ ·O·CH ₂ O...—OCH ₂ ·OH—sulphuric ester of polyoxymethylene	soluble
γ -polyoxymethylene CH ₃ O·CH ₂ O...—OCH ₂ ·OCH ₃ —polyoxymethylene dimethyl ether	insoluble

In all the products the degree of polymerization is high. At least 50-100 formaldehyde molecules (mol. wt. *circa* 6,000) are linked in a chain. Generally the polyoxymethylenes are crystalline and give definite Debye-Scherrer patterns; some can be obtained in thread form and give good thread diagrams (Faserdiagramme).¹

It is evident that the chains are composed of molecules joined by primary links, and that the auxiliary valencies are not involved in the polymerization. These highly polymerized substances are not homogeneous in the sense that all the molecules are equal in length and molecular weight. In the polyoxymethylenes the principal valencies are involved only in the direction of the length of the chain; in other directions the forces concerned are intermolecular and of the order of van der Waals forces (see p. 491). The special name, *crystallite*, is used to describe crystalline materials of this type, which consist of unequal, large 'macromolecules'. A bundle of rod-like chains of different lengths would form a crystallite. A further question concerns the mechanism by which the crystals of the poly-

oxymethylenes are built up. In the lower members of the series, which exist in solution as well as in the solid state, crystal formation follows the normal course, but a different state of affairs is found in the highly polymerized members. Here (according to Staudinger) the extremely long molecules, which make the crystals, cannot exist in solution, but break up into smaller fragments as the result of Brownian movement. The formation of crystals containing molecules of high molecular weight cannot, therefore, take place in the ordinary way, by deposition from solution, but must involve the addition of formaldehyde molecules to polyoxymethylene crystals, directly from the gaseous phase or from solution, containing short chains; this addition is followed by a topo-chemical reaction which involves the rearrangement of normal valencies and leads to the formation of a substance with a longer chain. It is important to note that the actual polymerization takes place in the solid state.²

There is definite evidence of the formation of long-chain crystallites, micelles in cellulose and its derivatives, as shown by X-ray investigations (General Discussion on the Colloid Aspects of Textile Materials and Related Topics in papers by S. E. Sheppard and J. J. Trillat, *Trans. Faraday Soc.*, Sept. 1932), so that Staudinger's implication is open to criticism.

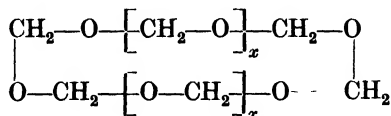
It has been suggested by Staudinger that the polyoxymethylenes may serve as a model for the explanation of the properties of cellulose. Cellulose, like polyoxymethylene, is crystalline and possesses a small elementary cell. Depolymerization may take place in certain solvents, because good solvating agents are capable of overcoming intermolecular forces of the polymeride and produce solvates. When dissolution occurs, a derivative is formed of lower molecular weight; the extent to which depolymerization has occurred governs the viscosity of the derivatives. A direct relationship between viscosity and molecular size is obscured by complications arising from a tendency to the formation of co-ordinate linkages. It has been pointed out that such a relationship cannot hold for aqueous starch solutions.³

Staudinger stresses the differences in physical properties (melting-point, solubility, strength (*festigkeit*), &c.) as due to the chain-length, whilst the chemical properties are dependent on the end-groups; cf. the following table:

	End-group		
α-polyoxymethylene (active, because of (OH) group)	HO—	CH ₂ —O—[CH ₂ —O] _x —CH ₂ O—	—H
γ-polyoxymethylene ether (inactive)	CH ₂ O—	CH ₂ —O—[CH ₂ —O] _x —CH ₂ —O	—CH ₃ } powdery
Hydrocarbon	CH ₃ —	CH ₂ —[CH ₂] _x —CH ₂ —CH ₃	—CH ₃ } paraffin-like
Alcohol	CH ₂ —	CH ₂ —[CH ₂] _x —CH ₂ —CH ₂ —	—OH } paraffin-like
Acid	CH ₂ —	CH ₂ —[CH ₂] _x —CH ₂ —CH ₂ —	—COOH } paraffin-like
		Chain-length determines physical properties	End-groups determine chemical properties

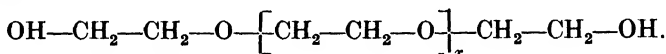
K. H. Meyer and H. Mark⁴ consider this too wide a generalization, e.g. in polypeptide esters with long chains the end groups have not a decisive influence on the chemical character.

At low temperatures formaldehyde may be polymerized to a solid form of high molecular weight. (eupolyoxymethylene) to which is ascribed a ring structure:

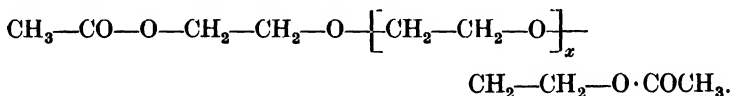


Polystyrenes. The polymerization of the polystyrenes has been discussed in Chapter V (cf. also p. 457).

Polyethylene Oxide (cf. Chapter XIII, p. 368). H. Staudinger and O. Schweitzer⁵ showed that a polymeric homologous series of polyethylene oxides could be obtained, whereby ethylene oxide* was polymerized under varying conditions. The physical properties varied with increasing mol. wt. and there was a relationship between the cryoscopic mol. wt. and the specific viscosity of solutions of equal concentrations. The polyethylene oxide was recognized as a dihydrate:

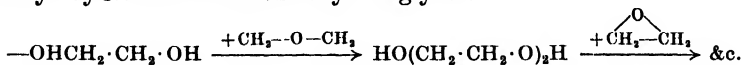


On acetylation diacetals are formed:



[M.W. 160–13,000, i.e. 3–300 polymerized units.]

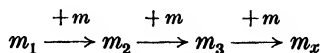
The polyoxyethylene chain is very stable in contrast to the polyoxymethylene chain. Staudinger considers polyoxyethylene as a model of starch, whereas polyoxymethylene is a model of cellulose. The polymerization of ethylene oxide has been recently studied by P. J. Flory⁶ by its reaction with ethylene glycol:



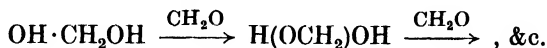
Ethylene oxide has been found to react similarly with alcohols, amines, mercaptans, and acids, yielding under proper conditions polymers of considerable length. In the patent literature there are described many technical processes in which polyethylene glycol chains are built up through the reaction of ethylene oxide with a substance containing an appropriate functional group (NH₂·NH, OH, SH or COOH). The available evidence indicates that these processes proceed exclusively by the reaction of monomer (ethylene oxide) with

* Direct oxidation of ethylene and other cheap olefines to the corresponding olefine oxides is now accomplished on the large scale by passing the gases mixed with air over a silver catalyst at high temperature (Carbide and Carbon Chem. Corp., B.P., 524,759.)

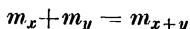
molecules possessing the propagating functional group, e.g. (OH) (chain polymerization), but reaction of polymer with polymer does not occur.



m_1 , the initial species bearing the propagating functional group m , ethylene oxide, m_x the product formed from m_1 plus $(x-1)$ ethylene oxides. Similarly, the formaldehyde polymerization, initiated by trace of moisture, proceeds as follows:

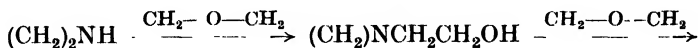


Similar mechanisms may account for the conversion of cyclic anhydrides,⁷ cyclic esters (lactones),⁸ and cyclic acetals,⁹ to the corresponding linear polymers. The distribution of species obtained by the above mechanism of polymerization and the distribution resulting from condensation polymerization are different (cf. pp. 424, 428). Condensation polymerizations, e.g. polymerization of a hydroxyacid, proceed by the occurrence of reactions of type:



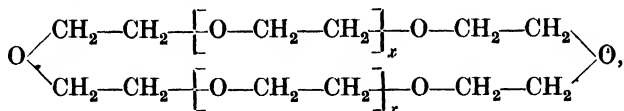
where m_x and m_y represent molecules composed of x and y units, x and y being integers from 1 to ∞ . Not only do the polymer molecules react with monomers, but polymers of all sizes react with other polymers. In all of these reactions the same chemical process is involved, and it has been demonstrated in the case of polyesterification that all of them proceed with equal ease.¹⁰

In cases where the initial propagating molecules are neither glycols nor alcohols, e.g. in the process:



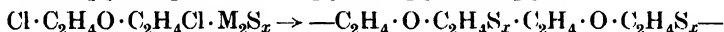
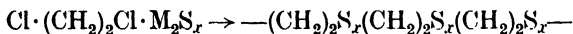
the rate of the first step will differ from the rates of subsequent steps, although the rates of the latter should not appreciably differ from one another. The first addition product $(\text{CH}_2)_2\text{N} \cdot \text{CH}_2\text{CH}_2\text{OH}$ must be considered as the initial chain propagator. Flory (loc. cit.) showed that in a polymer formed exclusively by the addition of monomers to a fixed number of polymer molecules, the numbers of species of various sizes are represented by Poisson's distribution law. Equations representing weight-fraction distributions have been derived, and the calculated weights per cent. of various species in several polymers having average sizes of 6 to 500 units were shown graphically. The distribution of these polymers typified by the polyethylene oxides has been contrasted with the distribution in condensation polymers (cf. pp. 424, 428). It would appear from Flory's work that the steric factor, so often referred to, is not a dominant factor in this

condensation. In polyethylene oxides the *solid* polymeride has a ring structure corresponding to the formula

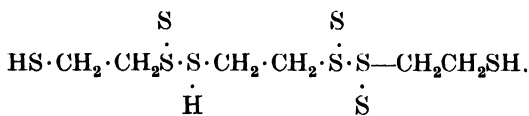


so that the properties of the end group are modified by the formation of ring-like structures. This closing of the ring and so influencing properties is of importance. The bearing of the polymerization of oxymethylene and oxyethylene on the *ad hoc* problems of resinification does not at first sight appear very close, but it is of historical interest, and the pioneer work of Staudinger dealt exhaustively with these substances, whereby the experience gained by investigation of these two systems has been of the greatest value in the development of the synthetic resin industry.

Thiokol Resins (cf. Chapter XIII, p. 349). An interesting type of multi-condensation leading to linear chains of high molecular weight is that which occurs between organic alkalides whose molecules terminate in CH_2X groups and metallic sulphides (thiokols); cf. p. 350 (M = monovalent metal).



The polymeric chain contains only 2 atoms of S per unit, the residual S (capable of removal and restoration) being probably co-ordinately bound.¹¹ The tentative formula for the rubbery tetrasulphide polymer is



HEMI-, MESO-, EU-, HOMO-, AND HETEROPOLAR-COLLOIDS

In *molecular* colloids the primary colloid particle is at the same time the molecule. These are to be distinguished from the *micellar* colloids, such as soaps, which are formed by association of particles with lower molecular weights. Amongst the molecular colloids three divisions must be recognized, Hemicolloids, Mesocolloids, and Eucolloids [Staudinger], it being always remembered that the dividing line between them must be indefinite, since the molecular colloids form a continuous series of gradually increasing molecular weight. When the molecular weight is relatively small, up to 10,000, corresponding to an order of polymerization equal to 20–100 chain length from 50–250 Å, the hemicolloids dissolve without swelling to give solutions

of *low viscosity* which obey Hagen-Poiseuille's law, and their filaments are of *low tensile strength*. When separated from solution they form powdery or glue-like masses. Staudinger recognizes a group of mesocolloids intermediate between hemi- and eu colloids, whose order of polymerization ranges from 100 to 1,000, their molecules having a length of 250 up to about 2,500 Å. They possess medium elastic tensile strength and medium viscosity in 2 per cent. solution. Before solution slight swelling occurs and they may be used for injection moulding. Eu colloids have macromolecules with a polymerization order over 1,000, the length of the molecules being over 2,500 Å. The longest thread molecules are those of the polystyrenes. They have a length *c.* 1.5μ and a diameter approximately 15 Å (Staudinger). The eu colloids have the characteristic properties of lyophilic colloids. Their dissolution is accompanied by intense swelling and their solutions are highly viscous, even at low concentrations; they do not obey Einstein's law and their flowing properties are not those of a normal liquid. The solid eu colloidal substances are tough and hard. The technically most important polymers belong to this group (Staudinger). They show high capacity for film formation and are often elastic. If eu colloids be subjected to a thermal cracking process or to a decomposition by oxidation, products with shorter molecules can be obtained, having mesocolloidal or hemicolloidal properties. The synthetic hemicolloids, e.g. hemicolloidal polystyrenes or polyvinyl acetates, are obtainable either by direct polymerization of the monomeric substance or by partial decomposition of the eu colloid. On the contrary, natural hemicolloids and mesocolloids can only be obtained by partial decomposition of the natural eu colloids, e.g. cellulose and its derivatives. Whereas some unsaturated compounds, e.g. styrene, acrylic esters, vinyl acetate, can give hemi-, meso-, or eu colloidal products, according to the special conditions of polymerization, some other compounds have so far yielded hemicolloidal products only. Indene, coumarone, and anethole ($C_8H_4(OCH_3)CH=CH(CH_3)$) give polymers with relatively short chain-length molecules only. The exact knowledge of the polymerization process is important from the technical point of view, the hemi- and eu colloids having different physical properties with different technical uses. For preparing varnishes hemicolloids are chiefly used, because the high viscosity is undesirable for the purpose. For artificial resins eu colloids are preferable because of their high tensile strength (Staudinger). It is doubtful, however, if this tripartite division will survive further work.

In homopolar molecular colloids (hydrocarbons, ethers, and esters, including caoutchouc and polystyrene) the thread molecules must show a length of 3,000 Å. The homopolar bond is that between two neutral atoms, where the so-called valence electrons form a pair and belong to both atomic nuclei in common (cf. p. 419). In the case of polystyrenes a polymerization degree of 1,500 would show eu colloid properties, whilst balata has a polymerization degree of 750. Both products contain 3,000 carbon chains, and have therefore a chain-

length of 3,400. The heteropolar molecular colloids such as sodium polyacrylate and proteins are soluble in water and have colloidal properties essentially different from those of the homopolar polymers, e.g. polystyrene or polyvinyl acetate. Their investigation has revealed much of importance for the understanding of the colloidal properties of solutions of cellulose xanthogenate or Schweitzer's solution of cellulose, as well as of protein, which are all heteropolar molecular colloids.

Heteropolar molecular colloids with a high molecular cation are the caoutchouc phosphonium salts. The heteropolar ionic bonds ('salt links of Astbury) are present between basic and acidic groups or as in NaCl depending on the mutual attraction between Na^+ and Cl^- ions [Houwink].

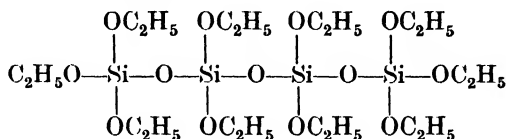
The eu colloids can, like the hemicolloids, be divided into homopolar, heteropolar, and co-ordinate (co-ordinate molecular colloids include polyvinyl alcohol, polyacrylic acid, cellulose, starch, and lichenin (see later)).

Meyer and Mark¹² draw attention to the views of Staudinger that eu colloids in solutions are split into isolated molecules and do not form associations (swarms or micelles). Staudinger has taken up this criticism and states that thread micelles exist in solution in soaps, and there are thread molecules in the case of rubber and polyvalent thread-ions in the case of sodium polyacrylate. In the opinion of the writer of this chapter much will depend on the character of the solvent. He considers that in certain solvents the formation of micelles is definite owing to the strong dipole character of the particles, whereas in solutions of different polarity macromolecules may be present whose length of chain is conditioned by steric factors. Although in many cases the evidence of the existence of macromolecules is strong, yet the existence of micelles cannot be ruled out as dipole attractions cannot be ignored (cf. p. 491). Micelles are particles of colloidal dimensions when such particles consist of more than one molecule, and the molecules cohere by means of secondary forces. This definition admits the possibility of the existence of molecules which may be even larger than micelles; such large molecules are *macromolecules*. The difference between a macromolecule and a micelle is that only primary bonds are present in a macromolecule (cf. p. 452) [Houwink].

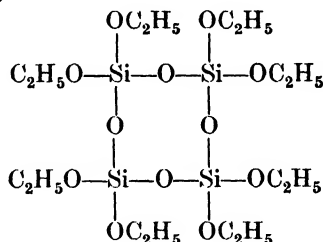
According to Haworth and Hirst (loc. cit.), the homopolar polymerides exemplified by the polystyrenes are comparatively simple cases of natural colloids, but much greater complexity of behaviour is shown by polymerides containing carboxyl, hydroxyl, or other reactive groups (cellulose, starch, &c.). The strong dipolar character of the substituent groups may result in the formation of co-ordinate linkages of the molecular chains, and the structure becomes 3-dimensional; when a molecule of this nature is found in solution, further complications may occur by the formation of co-ordinate linkings between molecule and solvent. It must be pointed out that these organic molecular colloids have no relationship to inorganic colloids

(colloidal metals); the latter are suspensoids or emulsoids formed by the splitting up into small particles. It is possible to obtain an organic suspensoid by dispersing it in a solvent in which it is insoluble, but such a suspensoid would be visible in the ultra-microscope. Colloidal solutions of organic compounds are optically empty and the colloid particles in them are identical with the molecules of the dissolved substance. This statement is now not correct. Many materials show bi-refraction and are anisotropically active. Herzog, Kratky, and Petertil¹³ utilize Tyndall light in the study of cellulose and polystyrol sols. Cf. also S. E. Sheppard and J. J. Trillat, loc. cit. (cf. p. 449). There is, however, one important inorganic molecular colloid, viz. silicic acid, which is similar in structure to polyacrylic acid.¹⁴

Silicon ester: *linear type*



Cross-linked type



Both the homopolar (e.g. polystyrenes) (molecules, in which all the atoms are bound by normal covalencies (Staudinger)) and the heteropolar molecular colloids (e.g. sodium salt of acrylic acid and the proteins) differ from the micellar varieties, the formation of which is due to intermolecular forces between comparatively small molecules and more particularly to the electric charges situated on ions.

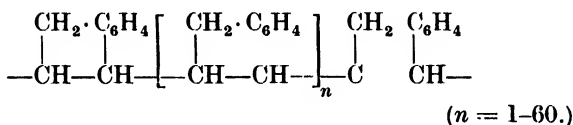
An important criticism for distinguishing between micellar colloids and molecular colloids is found in the observation that the former can usually be transformed into derivatives with normal solubilities, whereas the latter invariably give derivatives which will dissolve as colloids. Further differences between the two classes are that soluble molecular colloids invariably yield colloid solutions, whereas association colloids give colloidal solutions in some solvents and not in others; moreover, molecular colloids, apart from 'cracking' phenomena, do not alter in size with temperature as do the micelles in an association colloid. Staudinger tends to regard the micellar colloids as of comparatively rare occurrence as compared with molecular

colloids. K. H. Meyer¹⁵ maintains that proteins, polysaccharides, and caoutchouc are built up as micelles, formed by the association of long chains of atoms, which in turn are linked by covalent bonds, and considers that micelle formation is not exceptional, e.g. tannin in water, higher hydrocarbons, substantive dyes, and lower fatty acids in water (Haworth and Hirst, loc. cit.).

The above digression, taken from Haworth and Hirst's summary of work on polymerization, up to 1929, will show how the problems of polymerization have to be attacked from a chemical as well as a colloidal standpoint. In varnish systems as well as in resins the problems of unsaturated linkages are much to the fore. The problems of micelles and molecular colloids are so interwoven that it is occasionally difficult to separate the two, but it will be advisable to continue the consideration of the molecular structure as far as it is known of the different types of resins already described.

POLYINDENES

G. S. Whitby and M. Katz¹⁶ have shown that on polymerization of indene by stannic chloride or antimony pentachloride the products are complex mixtures: the lower the temperature of production the greater is the complexity of the product, and the polymerides show an unbroken series with a smooth relation between melting-points and molecular weights. The polyindene molecule, irrespective of the molecular weight, combines with 2 atoms of bromine, and therefore each polymer contains a double linkage indicating the formula:



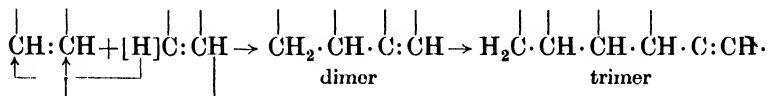
The double bond becomes less reactive the higher the degree of polymerization.

H. Staudinger and collaborators¹⁷ by the examination of polymerization of indene by catalysts (stannic, titanium, boron, and antimony chlorides) in benzene or chloroform solution, have isolated hemicolloidal polyindenes with a polymerization degree of 14-52 as a white powder with a mol. wt. 2,000-5,000. The viscosities of solutions of indene and styrene are similar in magnitude and indicate similar molecular structure in the two polymers, homologous series. Polyindenes, unlike polystyrenes, do not undergo ozonolysis, and the product is a mixture of polymerized monoxide and dioxide. Polystyrenes and polyindenes are probably formed from long chains, the terminal valencies of which become saturated by forming rings. No polyindenes were obtained which showed crystalline structure under X-ray examination (cf. p. 501).

G. S. Whitby and M. Katz¹⁸ have examined the polymerization

of polyindenes, especially di-indene. Di-indene polymerizes under the same conditions as indene, but more slowly. Di-indene and indene heated together at 177° for 15 days gave 33 per cent., and at 197° for 5.5 days 46.6 per cent., tri-indene. Higher polymers, when heated at temperatures below that necessary for pyrolysis, give compounds approximately $(C_8H_9)_6$. Pyrolytic distillation of di-indene at 2 mm. gave 74 per cent. indene. Bromine absorption showed the presence of one double linkage in all the polyindenes examined. It is considered that the polyindenes are straight-chain compounds (cf. Staudinger, *loc. cit.*), their formation involving the wandering of a hydrogen atom and addition to a double linking.

Whitby¹⁹ represents the formation of the polymers of indene, including compounds containing a conjugated system, especially butadienoid hydrocarbons and compounds containing a semi-benzenoid system, according to the following scheme:



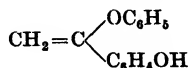
R. Signer²⁰ from an examination of the double refraction of the flowing solutions of polystyrenes in chloroform, benzene, &c., and of their behaviour in Svedberg's ultracentrifuge, concludes that the polystyrene molecules are more or less linear (cf. also pp. 450, 507).

Pyrolysis follows a reverse change and may take place in any part of the chain or in more than one place at a time.

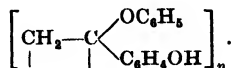
BAKELITE RESINS

The theory of the reaction between phenol and formaldehyde has been discussed in Chapter III, p. 113, but it must be confessed that the last word has not been said thereon and it is advisable to state the opinions of other investigators. There is general agreement on chain structure for the thermoplastic section and for cross linkages in the thermo-hardening class, but fuller explanation of the physical properties of these resins involves further factors.

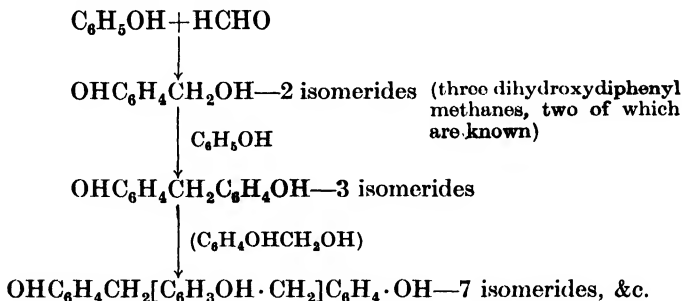
Backeland and Bender considered phenol-resinoid A to be:



and phenol-resinoid C to be:



It must be mentioned that in the interaction of phenol and formaldehyde many isomerides are possible, e.g.

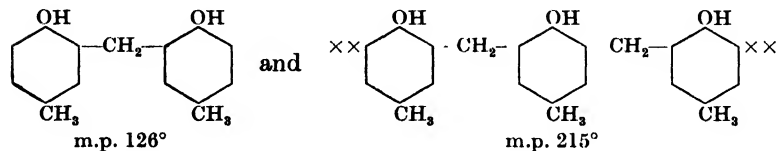


m-cresol may form six isomeric products, of which two are known. *m*-5-xylenol resembles phenol in number of condensation products; three possible dihydroxydixylyl-methanes have been isolated.

For each $[\text{C}_6\text{H}_3\text{OH} \cdot \text{CH}_2]$ *p*-cresol gives one isomeride, which may account for its generally unsatisfactory resins (Plastics Exhibition, South Kensington, 1932).

It may be pointed out that differences of the A, B, C varieties of bakelite may also be ascribed to the average molecular size resulting from extensive condensation.

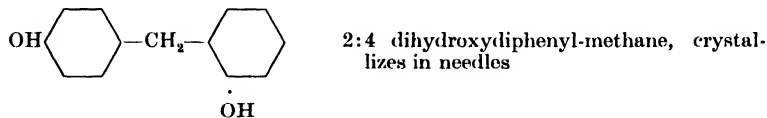
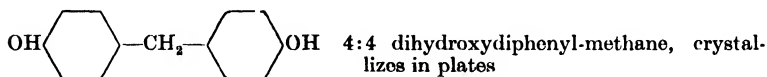
M. Koebner²¹ postulates a chain structure of the phenol-formaldehyde polymerization and discusses the effect of chain-lengths and of the presence of definite groupings in the molecule upon the chemical properties. The study of the constitution of intermediate crystalline products, when these can be obtained, furnishes the best method of elucidating the structure of the more complex resinous bodies. When the number of aryl groups in the chain is above 7, the compound is not soluble in caustic soda. With many-numbered chains water-insoluble sodium salts are produced.



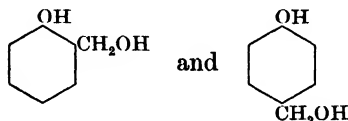
The explanation of the insolubility of resite in alkali and of the different properties of novolak and resite is considered to be in the length of their chains.

Megson and Drummond²² find that the condensation is best controlled by carrying out the reaction in the presence of organic solvents of suitable boiling-points. They conclude that the action proceeds through the formation of phenol rings linked by methylene groups. When the condensation was in alcoholic solution in the presence of hydrochloric acid, crystalline products containing 2 or

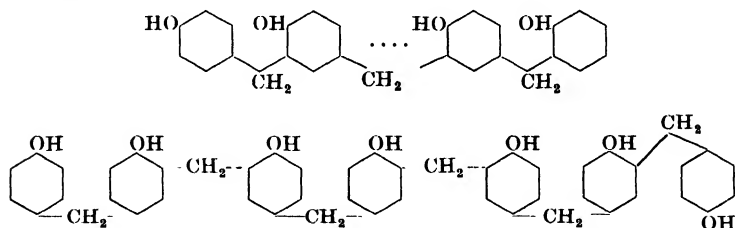
3 cresol groups were identified, e.g. with phenol 4:4 and 2:4 dihydroxydiphenyl-methanes were formed, and when the condensation was prolonged, the yield of the latter substance was reduced; therefore the 2:4 substance contributes to the formation of the resin. When phenol was replaced by *o*-cresol, the only intermediate product was 4:4 dihydroxy-3:3 dimethyl-diphenyl-methane.



Using alkaline catalysts *o*- and *p*-hydroxybenzyl alcohols (saligenin) were isolated.

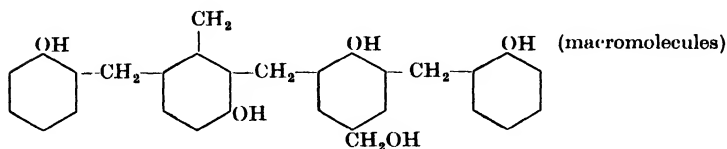
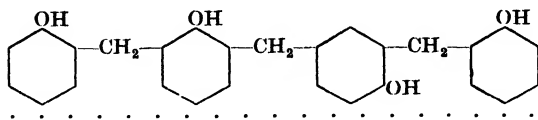


Pollak and Riesenfeld assigned the following formulae to the novolaks:



They conclude that by basic condensation of phenol and formaldehyde there are formed initially proportionally low molecular products, which have a strong polar character, and can be considered as dipoles as it appears from electric measurements. The further polymerization and association proceed slowly with rise of temperature, which is noticeable in the change of 'cementing strength'. *m*-Cresol reacts the best of the cresol resins and the dielectric constant increases with the phenol content. The reaction between cresol and formaldehyde leads to high molecular substances which have no polar character, as shown by dielectric measurements. Association to high polymers proceeds rapidly and proportionally. In mixed cresol and phenol resins the greater the phenol content the more marked are the phenol-resin properties; cf. the measure of the breakdown resistance and the *Spannungsabhängigkeit* of the dielectric loss. When the phenol percentage exceeds 30 the influence of the phenol

Resoles are mono- or polyalcohols of compounds of Types III or IIIA, and are produced by alkaline condensations.



Resites are irreversible structures made up of branched-chain macromolecules (see above). The latter may be united by primary

chains of alternate rings and methylene groups capable of being united by cross-linkages of the same groups (cf. Chapter III, p. 115).²⁶ This view is against that of Baekeland and Bender,²⁷ but it has had experimental support from I. Allen, V. E. Meharg, and

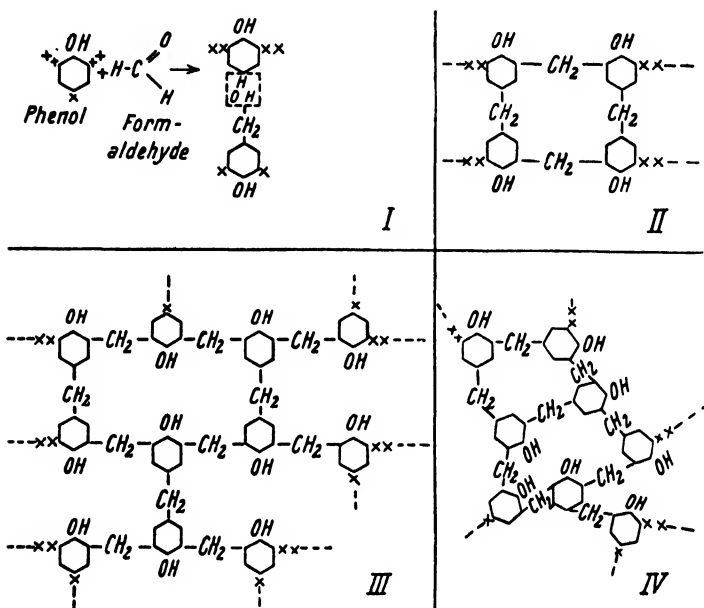


FIG. 46. A scheme for the phenol-formaldehyde reaction (Houwink)

J. H. Schmidt,²⁸ who report that after autoclaving a phenolic resin at 300° with caustic soda, the product contains phenols of higher boiling-point than that of the phenols used in its preparation. Such a result is consistent with the long-chain hypothesis on the assumption that rupture of the chain may occur on either side of a methylene group.

According to Weith (loc. cit.) the reaction scheme of Koebner²¹ has been widely accepted and, when taken in the light of the present understanding of the action of catalysts, gives a satisfactory picture of phenol-formaldehyde resinoids.

The influence of secondary linkages resulting from the strong polar (OH) groups or the weaker (CH₂) groups must be considered, so that the macromolecules can easily build complexes. For such secondary linkages the distances of two atomic centres would be 3-4 Å, whereas the primary linkages would give distances of 1.2-1.66. The further the condensation proceeds more micelles become co-opted

by atomic union to give macromolecules (cf. p. 460), whereby the secondary becomes a primary union.

The resistance of the resites to chemical attack may be explained as above without special chemical changes, e.g. disappearance of OH. The reactive parts are enclosed in the macromolecule.²⁰

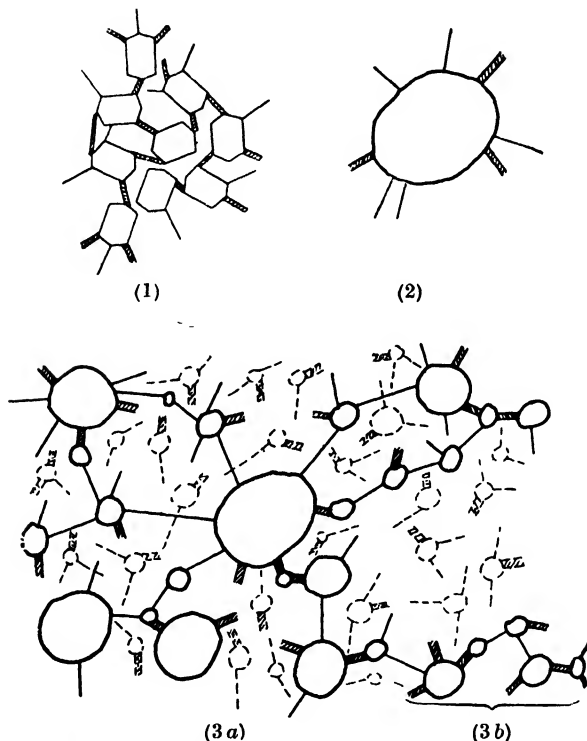


FIG. 47. Diagrammatic structure of the isogel of a thermo-hardening resin (Houwink)

This representation is very diagrammatic. The benzene nuclei must be imagined to be linked in three dimensions, but not in a regular manner.

Scheme IV (Fig. 46) is preferred to Scheme III, because no regular arrangement of the macromolecules can be established; moreover, the schemes illustrated must be considered as three-dimensional.

▣ Primary linkages (atomic distances 1.2–1.6 Å).

— Secondary linkages (atomic distances 3–4 Å).

○ Free fluid component.

(1) Micelle as macromolecule (cf. Scheme IV).

(2) Micelle as macromolecule; exaggerated.

(3) (a) isogel resin; (b) fringe of the complex.

In the case of a non-hardening resin, e.g. *p*-cresol resin, if once a ring be formed no more atomic union is possible, and although

The optical refraction of resins in relation to the chemical mechanism of resinification as studied by Houwink will be referred to in Appendix II.

N. J. Megson³¹ summarizes the present position (1939) of novolaks as follows:

Despite the difficulty of disproving the conclusions of Baekeland and Bender, who regarded novolaks as best represented by a phenoxyhydroxyphenyl-methane structure, present views incline to Scheme I, which satisfactorily explains the formation of the fusible, soluble type of resin.

Scheme I

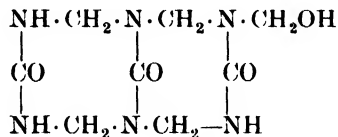
1. $R \cdot OH + CH_2O \rightarrow HO \cdot R' \cdot CH_2OH$ (phenolic alcohols).
- 1 a. $R \cdot OH + xCH_2O \rightarrow HO \cdot R' \cdot (CH_2OH)_x$ (phenolic polyalcohols).
2. $HO \cdot R' \cdot CH_2OH + R \cdot OH \rightarrow HO \cdot R' \cdot CH_2 \cdot R' \cdot OH + H_2O$
(dihydroxydiaryl-methanes).
3. $HO \cdot R' \cdot CH_2 \cdot R' \cdot OH + CH_2O \rightarrow HO \cdot R' \cdot CH_2 \cdot R' \cdot (OH) \cdot CH_2OH$
(alcohol of dihydroxydiaryl-methanes).
4. $HO \cdot R' \cdot CH_2 \cdot R'' \cdot (OH) \cdot CH_2OH + R \cdot OH$
 $\rightarrow HO \cdot R' \cdot CH_2 \cdot R'' \cdot (OH) \cdot CH_2 \cdot R' \cdot OH$ (trinuclear compound).
5. In general:—
 $x \cdot R \cdot OH + (x-1)CH_2O \rightarrow HO \cdot R' \cdot CH_2 \cdot (R''(OH) \cdot CH_2)_{x-2} \cdot R' \cdot OH$
(polynuclear chain compound) + $(x-1)H_2O$.

The process consists essentially of the entry of formaldehyde into phenolic nuclei to form alcohols, followed by condensation with more phenol. The polynuclear chain compounds cannot be called polymerides, since their production involves elimination of water, and they are not reversible. It is not considered that a novolak can be represented by any one particular polynuclear compound; it will be made up of a complex mixture of such compounds, and possibly their alcohols, and its molecular weight will be the mean value of the molecular weights of its constituents. This complexity is increased by the presence of numerous isomerides of the polynuclear type of substance, the only phenols in which this type of complexity does not arise being certain of those which contain but two or less *o-p*-positions available for substitution (e.g. *p*-cresol, *m*-2-xyleneol). Such a complex mixture will form a system in which crystallization of individuals will be difficult, and hence the resinous state will be the stable one. Raschig, and later Blumfeldt, came close to the truth in their speculations, which were, however, made at a time when reliable experimental evidence was not available.

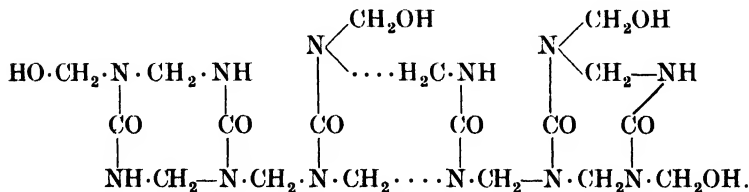
In later papers Megson concludes that dihydroxydiaryl derivatives (No. 2, Scheme I) can definitely be regarded as intermediate compounds in resin formation, since their yield decreases with time of condensation while that of the resin increases. Different mechanisms must be postulated for phenols, e.g. phenol and *m*-cresol, compared with bifunctional, e.g. *o*- and *p*-cresols. The difference has been explained as depending on the capacity for alcohol formation of the

moderation of the reaction to prevent the formation of methylol-methylene-urea consists in the use of small quantities of condensing agents or in the use of excess of formaldehyde. Under these moderated conditions there is no separation of the insoluble amorphous methylolmethylene-urea, but the formation of colloid solutions or fluids capable of passing to resin products. The formation of colloids in the place of methylolmethylene-urea (which forms in strongly acid media or by heating dimethylolurea without condensation agents) depends on the maintenance of an optimum H-ion concentration of 10^{-4} to 10^{-3} in aqueous solution; excess of formaldehyde acts as a peptizer.

Walter (loc. cit.) investigated the melting of dimethylolurea in the presence of various condensing agents; the formaldehyde evolved was determined and the resulting resin investigated. Since the experiments were performed in the absence of solvents, they were considered to be very suitable towards the elucidation of the change. In the absence of condensing agents 1 water molecule per urea molecule was split off with the loss of $\frac{1}{2}$ mol. formaldehyde. With condensing agents the water evolved increased as the formaldehyde fell, so that 1.4 water molecules and 0.2 mol. formaldehyde were split off. He concluded that, taking as a basis the losses of water and formaldehyde given above, there will be a regular structure through an average 3-member ring chain which has a free methylol group.



[I] [3-membered ring chain]



[III]

The two (OH) groups in dimethylolurea may be partly responsible for the hydrophilic properties of the gel. On prolonged heating condensation may lead to the formation of very large macromolecules containing fewer (OH) groups, so that their hydrophilic properties will be greatly reduced.⁴¹

On the supposition of an irregular structure the number of members is indeterminable by the water values, and there can be constructed in place of a 1-dimensional chain a 2- or 3-dimen-

sional picture. An increase in the number of urea residues per resin molecule where the number is 10 is shown as [II], the middle formaldehyde residue does not pass into a methylene bridge, but is split off or remains as a methylol group. The results indicate a regular low molecular structure for the resin. The author was able to show that the water-insoluble methylolmethylene-urea passed easily into solution in formaldehyde and in the hot press gave in a few minutes a white resinous product, whereby the methylol groups came into action with the splitting off of water as indicated in [II]. From the experimental results the author concluded:

(1) H-ions act as splitting off water and formaldehyde. Small H-ion concentration (10^{-4}) acts dehydrating, but with less removal of formaldehyde.

(2) The action of increased (OH) ion concentration resembles the action of the lower H-ion concentration with less loss of formaldehyde (chain and resin formation). This discovery that H-ions act as water- and formaldehyde-removers and that (OH) ions act chiefly as water-removing is in agreement with A. Einhorn's work, in which he showed that methylolpropionamide in the presence of acids gave a methyl-bis-azyl compound, but in the presence of bases the methylolmethylene-bis-azyl compound was formed.⁴²

A similar investigation was made with thio-urea, and the results pointed to low molecular representation. Walter maintains that the urea-formaldehyde colloids are built up of low molecular structures and are not like the thread molecules of Staudinger's polystyrenes. The number of members in the series is to be considered not more than 10 in number. They are therefore not the results of *polymerization* but of *condensation* phenomena by the linking up of methylol ureas with loss of water.

The hardening by heat (of the urea-formaldehyde resins) may also be ascribed to strong secondary linkages for which the amino, methyl groups and the dipole moments of the free urea may be responsible.⁴³

In a subsequent paper on the study of complex ions of the urea-formaldehyde condensations Walter⁴³ concludes that from the comparison of electrical conductivities of monomeric and polymeric methylene-ureas in formic acid with the results of the direct determination of the molecular weights in the same solvent, as well as with those of the determination of primary NH_2 end-groups shows that complex ions must be present in these solutions.

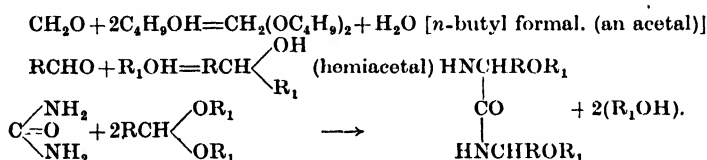
In the formation of complexes the increase in the number of particles due to electrolytical dissociation is always exactly counter-balanced by the decrease due to the production of complexes. Direct determinations of molecular weight give, therefore, results which show no signs of electrolytical dissociation. Only from the results of all three methods together—determination of the end-groups, conductivity, and molecular weight—is it possible to show the formation

of complexes. The equivalent conductivity varies with the degree of polymerization and with the nature of the substituents in the amido group. The influence of positive and negative substituents has been examined.

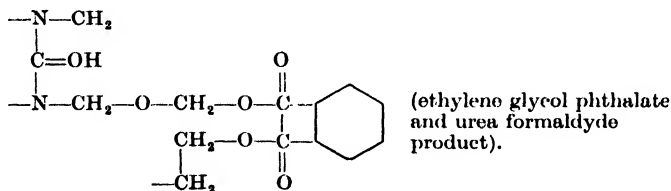
The degree of complexity increases with growing polymerization. The complexity can, however, obtain remarkable values even at very low polymerizations under certain conditions.

The formation of complex ions makes the equivalent conductivity of the methylene-urea formates appear low as compared with that of other formates.

Since Walter's conclusions the subject has been discussed by F. S. Hodgins and H. G. Hervey,⁴⁴ who has reviewed also the conclusions of Staudinger⁴⁵ Redfarn,⁴⁶ and Carleton Ellis.⁴⁷ The resulting condensation product is dependent on (a) the catalyst employed, including the pH of the solution; (b) the molecular ratio of the reacting components; (c) the time and temperature of the reaction. Hodgins and Hervey have included acetal and hemi-acetal reactions in the presence of monohydric alcohols (*n*-butyl alcohol).

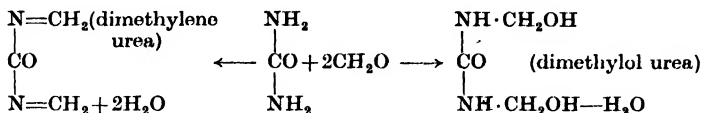


This has been extended to the condensation of urea with complexes of a polyhydric alcohol and polybasic acids

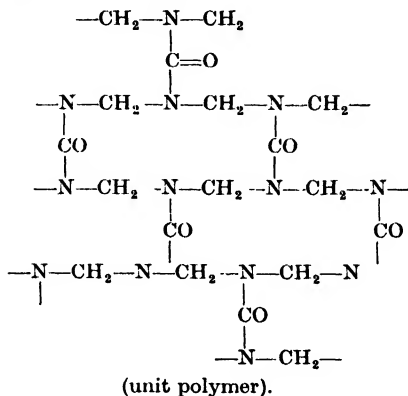


The acetal products are film forming and are soluble in *n*-butyl alcohol, and the solution is miscible in hydrocarbon solvents and also compatible with nitro- and ethyl-cellulose. The thermo-hardening property is due to a three-dimensional structure. Monomethylurea containing only one CH₂OH gives only chain polymers which do not gel, whereas dimethylolurea with two CH₂OH groups gels. One mol. urea and one mol. CH₂O giving the monomethylol urea does not gel; whereas, if CH₂O : urea be (1 : 1), the tendency for formation of the three-dimensional condensation product is increased. Hodgins and Hervey propose the following formula in preference to those of Redfarn and Ellis and Walter as showing the three-dimensional character of the molecule more clearly in the thermo-hardening

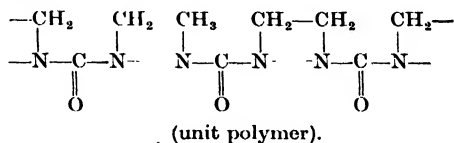
varieties, but Walter restricts the number of interacting units to ten.



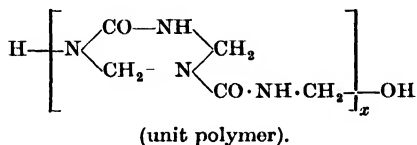
Hodgins and Hervey.



Redfarn.



Ellis.



Polymerization of vinyl acetate and vinyl alcohol. The polymerization of these substances has been discussed in Chapter V, p. 192.

SUPERPOLYMERS

In the previous chapter, p. 437 a description was given of the work of Carothers and Arvin on the condensation polymerization of the esters of dibasic acids and dihydric alcohols.

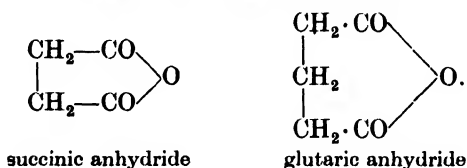
By the use of the *molecular still*⁴⁸ in reversible reactions involving the simultaneous formation of volatile and non-volatile products, substances have been obtained of a yet longer molecule by the elimination of a volatile product.⁴⁹ Superpolyesters (ω form) have been produced in contrast with α -esters with molecular weights 800-5,000 from dibasic acids and glycols (see above). They are tough, opaque solids, which show a definite X-ray powder-diffraction pattern.

α - and ω -Polyesters from Trimethylene Glycol and Hexamethylene Dicarboxylic Acid

	α -Ester	ω -Ester
Apparent mol. wt.	3,000	12,000
At 100° C.	viscous liquid (d^{20} 1.061)	opaque, elastic, horny (d^{20} 1.058)
At room temp.	white, opaque, brittle wax	elastic, opaque, horny, and cream coloured
Melting-point	75-76°	transparent at 75°, but does not flow
Solubility	very soluble in CHCl_3	Swells in CHCl_3 and then dissolves
	Viscosity (7.3%) = 8.6 units	Viscosity (7.3%) = 166 units

Anhydrides of the acids of the series $\text{HO}\cdot\text{OC}(\text{CH}_2)_x\text{COOH}$ are known in which x has values from 1 to 8 inclusive. $-\text{CH}_2-$ is the structural unit (a bifunctional substance).

Of these, only succinic and glutaric anhydride are monomeric, which are effectively 5 and 6 rings. The other anhydrides, containing 7, 8, 9, 10, and 11 rings, are all highly polymeric.



In another paper⁵⁰ sebacic α -anhydride (m.p. 79-80°) formed by the action of acetic anhydride on the acid was found to be a linear polymer with open chains and molecular weight about 5,000, $\text{CH}_3\text{CO}-[\text{O}-\text{CO}-(\text{CH}_2)_8-\text{CO}]_x-\text{O}-\text{CO}-\text{CH}_3$, which shows acetyl groups as terminals. In the molecular still the α -anhydride yielded an ω -anhydride, a polymer of much higher molecular weight, which is very tough and, when freshly prepared, can be drawn out into strong pliable lustrous oriented fibres and a definitely crystalline volatile β -anhydride, m.p. 68°, which is a cyclic dimer (mol. wt. 368). The β -anhydride above its melting-point polymerizes, giving a γ -anhydride, m.p. 82°, resembling the α -anhydride.

The linear condensations of ω -polyesters, polyanhydrides, and

mixed ester polyamides are easily drawn out into very strong, pliable, oriented fibres resembling those of silk and cellulose.

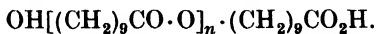
Fibre strength should depend on molecular length, and Carothers states that continuous filaments of hydroxydecanoic anhydride require mol. wt. 7,000, and cold-drawn fibres 9,000. He concludes that for strength and plasticity the molecular weight should be 12,000 and molecular length at least 1,000 Å. Linear condensation-



FIG. 50. Filaments of 3-16 ω -ester spun from chloroform solution showing transparent fibres produced by cold drawing ($\times 15$)

polymers are generally crystalline, unless bulky substituents are present to destroy the linear symmetry of the chains: addition-polymers of vinyl compounds are more rarely crystalline, because they are probably 3-dimensional polymers (but cf. p. 195). 3-dimensional polymers are unsuited for fibre orientation. According to Carothers glyptal resins belong to this class, because they give fragile threads and show no sign of orientation when examined by X-rays.⁵¹

By condensation polymerization W. H. Carothers and F. J. van Natta⁵² have prepared from *l*-hydroxydecoic acid a series of polyesters (M.W. 2,780-25,200) of the type



Strong orientated fibres are obtained only from esters of molecular weight greater than 9,330.

J. W. Hill and W. H. Carothers⁵³ have produced from the acids $(\text{CH}_2)_n(\text{CO}_2\text{H})_2$ [$n = 4-12$ and 16], by heating with acetic anhydride, linear polymerides of α -anhydride (M.W. 3,000-5,000) of the type $\cdot\text{O}\cdot\text{CO}\cdot[\text{CH}_2]_n\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot[\text{CH}_2]_n\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot[\text{CH}_2]_n\cdot\text{CO}\cdot$. In the molecular still volatile β -anhydrides (fluid cyclic monomerides or crystalline dimeric anhydrides) and more complex ω -anhydrides are

produced, which are tough, opaque solids capable of being drawn into highly orientated films; these, when heated long enough in the molecular still, are converted into β -anhydrides. When linear polyesters of unit length greater than 7 are heated at 200–250° under conditions of molecular distillation; the chains couple to form longer chains. The polyesters (M.W. 10,000) can be drawn into tough, pliable forms. It was recognized that depolymerization might occur in the molecular still as in the case of 6-membered cyclic esters.⁵⁴

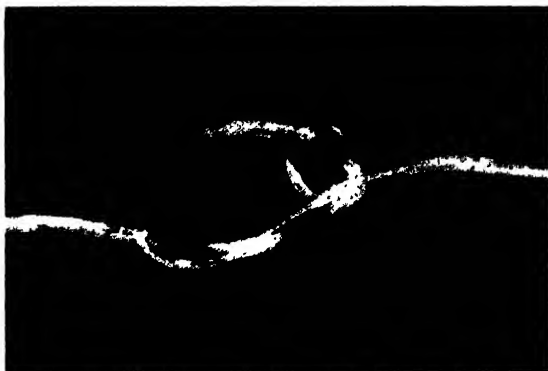
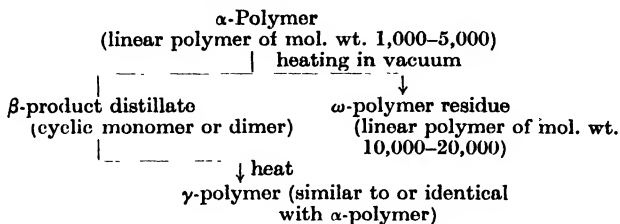


FIG. 51. Cold-drawn fibre from ω -anhydride of decamethylene dicarboxylic acid. The lack of definition is due to specular reflection caused by high lustre

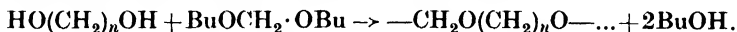
Polymeric methylene carbonates, prepared from $(\text{CH}_2)_n(\text{OH})$ ($n = 5, 7-9, 11-14, \text{ and } 18$), butyl carbonate, and a little sodium at 170°, are depolymerized by heating with catalysts in a vacuum,⁵⁵ and under certain conditions smooth depolymerization to the corresponding monomerides or dimeric esters occurs; the method makes it possible to obtain for the first time monocyclic esters in good yields. The macrocyclic esters and anhydrides of the two preceding papers have odours of musk-like character, resembling those of ketones and lactones of the same ring size. The rings in the neighbourhood of 15 atoms all have musk-like odours.⁵⁶ The formation of large ring ketones is considered to involve the intermediate production of a linear polyketone, which then decomposes; the changes are similar to those for esters and anhydrides (above). Rings of more than 5 atoms are not regarded as strainless, and the authors discuss the probable nature of the strain in large rings.⁵⁷ Bifunctional esterifications generally yield cyclic monomerides or linear polyesters, depending on the reactant (most important), the nature of the unit, and the experimental conditions, especially dilution. It is well known that substituents (e.g. methyl) favour ring closure. The simplest possible structural situation for self-esterification is found in the ω -hydroxy-acids, which have been investigated for the first time;

ϵ -hexolactone has been prepared and its behaviour compared with that of other cyclic or polyesters.



Polyanhydrides are depolymerized more readily than esters.

Polyformals obtained by interaction of a glycol with dibutyl formal yield β (cyclic monomer and dimer) and ω forms



Decamethylene formal yielded 25 per cent. of a volatile cyclic dimer and the residue could be cold drawn to give a tough fibre.⁵³

The summary of Carothers's work is of great interest. It shows the co-operation of chemical and physical methods and the influence of structure of the molecule on the polymerization. Although technical resins are not dealt with, his synthetic methods have produced substances with resin-like characteristics, and therefore the writer of this chapter considers the digression to be justifiable. The colloidal state is carefully investigated and the terms micelles, swarms, secondary valencies are not used in the sometimes indefinite manner of investigators. In a later communication he considers that the Svedberg ultracentrifuge provides the only means yet available for determining both the average molecular weight of polymers and the distribution in polymeric mixtures. The viscosity methods are of value as a means of providing rough estimates concerning the relative order of magnitude of molecular weights in a given polymeric series. In dilute solutions the error is less, but high polymers are generally mixtures covering a wide range of molecular species.⁵⁹

POLYAMIDES

Similar work to that on the polymerization of hydroxy-esters has been carried out with polymers of amino-acids and of diamines with di-acids. The amino-acid condensation corresponds to that of the hydroxy-ester, while the formation of polyamides corresponds to the formation of polyesters. In all cases the formation of both ordinary polymers and *super*-polymers is possible. Thus the dehydration of amino-caproic acid under normal conditions leads to a polymer of molecular weight about 2,000 and having the following structural unit:



Further dehydration processes carried out by means of molecular

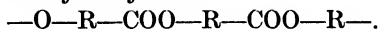
distillation or treatment under pressure lead to *super*-polymers of much greater toughness and hardness.

The relation between these various types of polymers is as follows :

(1) Polyester from acid and alcohol :



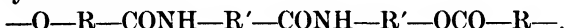
(2) Polyester from hydroxy acids :



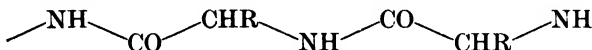
(3) Polyamide :



(4) Polyester amide :



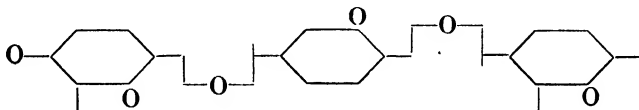
It will be seen that type (3) is closely related in structure to natural proteins. Certain of these can be spun into fibres, and the essential structure of these materials is as follows:⁶⁰



In the case of silk the group R is chiefly methyl, while in the case of wool R represents a complex mixture of amino-acids.

It is probable, therefore, that *super*-polymers of type (3) will be capable of being spun into fibres. In fact it has been found possible to spin fibres from polymeric materials of all the types. The development of these synthetic fibres marks the culmination of the work of Carothers and his school on polymerization.

The products of polymerizations of type (3) have been found to be suitable for the development of synthetic textiles. The new synthetic products are clearly more closely related to silk and wool than to cellulose materials such as cotton, as can be seen from a consideration of the structural unit of cellulose :



The disposition of the CO and NH groups of polyamides and the configuration of the group R between these affects markedly the nature of the material obtained, especially its capacity to form fibres which can be spun. It is possible to produce fibres of simple materials like polyethylene and a very great variety of other materials. None of these are of suitable structure which will enable them to be spun so as to compete with natural fibres.

As mentioned above, *super*-polymers of suitable structure are now used as the basis of synthetic fibres. The generic term 'Nylon' has been applied to materials of this type. The number of Nylon polymers is unlimited and the term includes materials made from

amines, amino-acids, and acids with all possible variations of chain length, of unit, &c. The properties of the polymer may be varied at will by alteration in the structural units employed.

The structure of a Nylon polymer for a specific purpose has not been disclosed, but the general method of preparation can be seen from B.P. 461,367;⁶¹ this discusses the condensation of long-chain diamines and di-acids, the limitations as regards the length of unit for a satisfactory product being noted. A suitable pair of reactants are hexamethylenediamine and adipic acid. A salt is first formed from such materials and this is then polymerized at a high temperature under pressure, under reduced pressure, or in the presence of high-boiling solvents.

The molten material so obtained is extruded as a ribbon and this is ground into granules. This material is crystalline and has a sharp melting-point. In the manufacture of fibre the granules are again melted and extruded through spinarets by a process known as melt spinning. The filament so obtained is then subjected to a cold drawing operation whereby molecular orientation occurs and the fibre takes on the characteristic properties of Nylon.

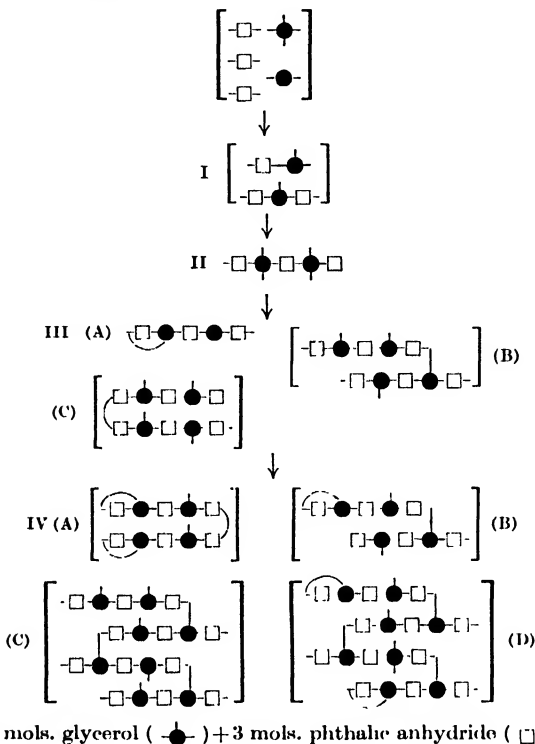
The synthetic fibres prepared as outlined above have very high elastic recovery and great tenacity. Their water absorption is also much less than natural fibres and they are also non-inflammable. As a result they are being most vigorously exploited in the development of synthetic textiles and in other uses. Their use as bristles in tooth-brushes is already well established, and other uses of thick fibres are receiving very active attention. In the field of textiles attention is probably being directed towards the production of stockings, thus competing with natural silk, rayon, and viscose. The relative merits of these fibres have been recently discussed by G. P. Hoff.⁶²

The materials hitherto described are too infusible and insoluble to be of use in coating compositions, but it is possible by a modification of the structural unit, especially by increasing the amount of oxygen in it, to develop materials soluble in ordinary solvents which may have a future in the field of coating compositions.

GLYCEROL PHTHALIC ANHYDRIDE RESINS

This class of resins has been discussed in Chapter XI with reference to the structure of resins formed by interaction of glycerol and phthalic anhydride or acid.⁶³ It is advisable to elaborate the conclusions of the above, briefly referred to in that chapter. On the basis of *inter*-esterification as the primary reaction with the anhydride, and *intra*-esterification as secondary reaction possibilities, it has been found possible to derive approximate theoretical compositions which satisfy all the determined values. In arriving at these calculations a scheme proving the structure and characteristics of four typical glycerol phthalate samples is shown in the following diagrams.

The compositions of the several glyceryl phthalate samples agree well with those calculated. Only when A.V. has reached a value 190



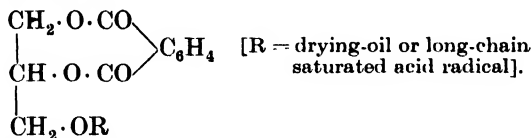
do molecules of species III appear. From this point to A.V. 135, molecules of species III are forming. Further on, molecules of species IV type with three-dimensional complexities begin to appear until their concentration is sufficiently great to cause gelation. The non-appearance of the complex three-dimensional type IV until A.V. 137 is reached offers an explanation for the change in specific viscosity at that stage. The introduction of the intra-esterification and anhydride modification accounts for the acid-value and water-loss relationship, because the water evolved is greater than that required for inter-esterification. The general schematic representation of the progress of the reaction presented above is consistent with experimental data. The reaction proceeds to the formation of a mixture of polymers, and gelation occurs when a sufficient complexity of three-dimensional molecules has been reached to bring about arrested motion. The gelation in polymerides is not necessarily attendant on the formation of gigantic macromolecules, but can occur by the inter-twining of three-dimensional molecules with a relatively low degree of polymerization.

*Calculated Composition of Various Glyceryl
Phthalates at 200°*

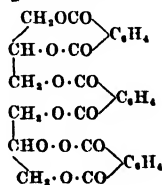
Observed	Species No.	Approx. mol. fraction	Calculated
A.V. = 235 Va. = 1.00cc. M. = 425	I	0.60	A.V. = 235 Va. = 1.80
	II	0.40	M. = 480 v. = 1.7
Mv. = 406 A.V. = 184 Va. = 3.80cc.	I	0.40	A.V. = 190
	II	0.30	Va. = 4.00
	III A	0.30	M. = 488 v. = 1.5
Mv. = 460* A.V. = 137 Va. = 6.70cc. M. = 795	II	0.33	A.V. = 140
	III A	0.33	Va. = 6.7
	III B	0.33	M. = 801 v. = 2.0
Mv. = 800* A.V. = 126 Va. = 7.60cc. M. = 1120 S.V. = 551 Mv. = 1150*	II	0.167	A.V. = 125
	III A	0.167	Va. = 7.60
	III B	0.333	M. = 1190
	IV A	0.084	S.V. = 552
	IV B	0.083	v. = 2.6
	IV C	0.084	v. = basicity
	IV D	0.083	Va. = H ₂ O evolved

* For details as to method of obtaining Mv. cf. Kienle (loc. cit.)

H. H. Morgan⁶⁴ distinguishes between glyptals of the straight type (cf. Hönel) and those of the oil-modified type (pp. 287-91). In the second type resins are produced which are oil-soluble, and it will be of interest to consider their formation in the light of the theories already advanced. In the oil-modified glyptals the general arrangement, according to Morgan, is represented as follows:



The straight glyptals are represented as:



The representations by Morgan must be considered as possible illustrations and do not imply reaction of equivalent proportions of phthalic anhydride, glycerol, and the drying-oil. The modification can proceed in any quantity between the extremes of an unmodified glyptal and a single drying-oil. Further, the position of the drying-oil is not defined; it may react either α - or β - to the glycerol according to the reaction temperatures and method of incorporation. The formula given by Morgan has been criticized by Wornum⁶⁵ because it is not in keeping with the current views of polymerization and resin formation. The influence of polymerization of the oil component must also be considered, because in the case of tung oil the more this has proceeded in the initial resin formation the less subsequent reaction is required in the drying stage.

The presence of the drying-oil introduces a factor of polymerization of *oxyns* as the governing factor. This polymerization will be referred to later (p. 504), so that representation on lines of Hönel's formula must be modified; yet it must be stressed that the influence of the glycerol on intramolecular association is very marked, therefore the association of *oxyns* and of the glycerol ester contribute to the complexity of the product. The modified glyptals, as above, containing also saturated long-chain acids, are non-oxygen-convertible, and so take longer to harden under the action of heat (100-120°) than the straight *oxyns*, but they do not discolour, because of the absence of *oxyns* which always show a tendency to darken on stoving.

F. J. Siddle⁶⁶ also criticizes Morgan's representation. In the consideration of functionality distinction should be made between groups in a molecule that actually function as reactive centres and those which are only potentially functional. Only when a group has intermolecular functionality can it function in building up a polymeride. In the alkyd resins the unsaturated bonds of the drying-oil acid are not functional and their oxidizable activity is fully retained. On the other hand, the unsaturated bond of dibasic acid may be reactive as in ethylene glycol and maleic acid, which react to give a product showing gelation and heat-hardening properties (cross-linkage to a three-dimensional structure) with comparative ease, i.e. the reaction is not bi-bi- but bi-tri-functional, the double bond in the maleic acid being a reactive centre as well as the carboxyl and hydroxyl groups. T. F. Bradley⁶⁷ suggests that polymerization of the maleic anhydride resins involves two types of reaction, viz. condensation and addition, the latter taking place only when condensation has progressed sufficiently far to provide a linear unit which has at least two double linkages per molecule. This view is supported by the preparation of thermo-hardening resins by interaction of a polyhydric alcohol with an unsaturated aliphatic polybasic acid in which a polymerization catalyst (benzoyl peroxide) is introduced after the initial condensation has ensued.⁶⁸ Moreover, there is a definite relation between heat conversion of a resin and its air-drying properties in film form and the same mechanism of gel formation, the

interlinking of chains by primary valence links is probably operative in both cases. For example, the mono- and di-glycerides of drying-oils, although polymerizable, do not air-dry, whereas the tri-glycerides have air-drying properties. The functional activity must be *three or more* to obtain thermo-hardening. Only in a very limited number of cases when a dihydric alcohol and a dibasic acid react is there *intra*-molecular condensation, the normal reaction being *inter*-molecular with the formation of long-chain polymeric esters. The introduction of glycerol gives a system capable of cross linking and the chains can be united to give a three-dimensional structure. With a dihydric alcohol the chain length ceases to grow in the case of glycol succinate after a chain length of about 20 units. When a third hydroxyl is introduced cross-linking occurs after 7 to 8 glyceryl phthalate units are formed. It is apparent that whereas in a bi-bi-reaction as polymerization proceeds there is no accumulation of unreacted or potentially functional groups, in a bi-tri-reaction there is an increasing accumulation as the polymer grows. Gelation is due not to the formation of a huge, many unit, macromolecule, but to molecular structures, whose comparatively small size is rendered compact and rigid by cross linkages and which includes a variety of molecular species (Siddle).

In the consideration of drying-oil alkyds it can be considered that the building up of the polymeride is analogous to the reaction of glycerol and succinic acid. If less than one molecule of drying-oil acid be present the structure tends more towards glyceryl phthalate; with increasing proportion of drying-oil acid the characteristics of a drying oil are approached. Although the reaction is one of esterification, the acid number is not a direct criterion, and two products of the same acid number may show different properties. The most remarkable difference between films of drying-oil alkyds and resin oil varnishes of comparable oil-length is shown in durability. A drying-oil alkyd has a bigger, more complex and closer knit molecular structure than a polymerized oil, and the glycerylphthalate part of the structure is non-oxidizable. Disintegration is slower and greater durability assured.

A general consideration of the structure of drying-oil alkyds compared with resin drying-oil mixings indicates a closer association of resin component in the former case, although in both cases the drying action is dependent on the double linkages of the unsaturated oil radical present in both, either as a complex glyceride or a simple glyceride. The durability of the oxyn from the unsaturated acid depends on its degree of oxidation.

It may be that ketol formation, which is usual in drying-oil oxidations, does not occur in the drying-oil alkyds. It is the ketols, in the opinion of the writer, which are the weak part of the drying-oil oxyn chain, owing to the breakdown by moisture in the presence of oxygen. This opinion might be confirmed by application of a new method of examination of the oxyns.⁶⁸ The correct view of the structure of the alkyd films cannot be settled until more is known of the structure of

micelles into coarser units or flocculates. These flocculates will also be reversible in character as long as secondary valency forces are involved. The secondary valency forces forming flocculates will be of a different order from those forming micelles, and redispersion to the micelle state will normally be accomplished more readily than redispersion from the micelle to the molecular stage. The final stage in colloidal complexity is the aggregation of the flocculates to the irreversible gel or solid resin state, wherein the primary valencies have come into action as in the example given above.

He considers further the properties of these flocculates or swarms, which give reversible or irreversible gels. Free fatty acids, resins, driers, are treated as dispersing or coagulating agents in terms of the author's theory. The webbing of tung oil is stated to be due to a random coagulation of large flocculates, whilst a crystalline appearance follows the attainment of partial orientation. In the heat-bodying of tung oil, at temperatures below 270° , the activity of the acid in the β position of the glyceride is insufficiently energized to allow primary-valency cross-linking to take place readily. It is not until 270° is reached that the conditions favouring cross-linking take place with reasonable ease at chance points of contact; at this temperature the conditions are directly favourable to flocculate growth. At 310° the rate of primary valency cross-linkage is greatly increased, and new flocculates are formed in a much larger number of smaller units. The unused β position of the glycerides in undercooked tung oil favours the formation of large flocculates, and hence webbing.

Investigation of the chemical changes ensuing on the gelation of tung oil and of β elaeostearin by heat or at the ordinary temperature by catalysts (methyl or ethyl sulphate) has shown that the liberation of energy on gelation is so great that an oxyn of a dimer is produced under either condition. Gelation in this case would seem primarily to be a process of oxidation of the dimer, and explanation by the character of flocculate formation alone requires study of the primary valency interaction.⁷²

Wornum divides varnishes into two classes, viz. those in which a disperse phase is constituted by a large number of small flocculates, and those characterized by a smaller number of large flocculates. The above conclusions on drying-oils and resins are supported in many respects by investigators of other systems. In the opinion of the writer, although there would seem to be evidence for a difference between the properties of the α - and β -hydroxyl groups of the glycerol radical, it is not yet proved that it is a dominant factor in the above changes. The components are of such complex composition (and, moreover, the influence of chemical structure is in many cases unknown) that the properties of aggregates, held together by adhesional or secondary valencies, must at present be considered solely from the colloid aspect. Further investigation on the structure and a better knowledge of the functions of the primary and secondary valencies must be co-ordinated to give a more complete picture of the changes than the colloid aspect alone can do.

Kienle⁷³ suggests a theory of gel formation depending on the bonding of macromolecules, whereby convertible or non-convertible polymers can be obtained by simply changing the number or position of reactive points in the interacting molecules. The ability of the gelled polymers to reconvert to the sol-state with proper swelling agents points to a colloid structure for glyceryl phthalates. He suggests interaction of simple molecules to produce a mixture of various-sized molecules. According as the molecules, through their primary valencies, are built up by intertwining, then convertible polymers will be formed. Whenever straight-chain unions occur, non-convertible polymers will be formed. A mixture of polymers may be obtained in which small molecules of low degrees of condensation are associated with large polymeric molecules (cf. Pollak and Riesenfeld on the phenol-formaldehyde resins, loc. cit.). With this conception Kienle states that nearly all the known formation reactions and sol-gel phenomena are intelligible, except polymers formed from highly polar ingredients, e.g. phenol-formaldehyde, aniline, and urea resins, although even here the concept in general holds. In these resins association forces seem to play a more important role during the sol-gel transition than otherwise. Such resins (urea) are hydrocolloidal systems owing to their water-medium formation. The importance of dehydration and of its bearing on gelation of these resins has long been recognized by those interested in their industrial development; in particular the work of Pollak and Ripper⁷⁴ refers to the proper dehydration of the urea resins. They showed that they are hydrocolloids, and applying known colloid treatment thereto a variety of products results. Recent work on aniline and phenolic resins points to the same conclusions. Kienle suggests that there are two aspects: viz. the formation of polymeric molecules is fundamentally a primary linking of molecules by primary valencies, but in one case during gelation the primary valence linkage is of fundamental importance, whilst the association forces (if acting at all) are of secondary importance; in the other case association forces are paramount.

GENERAL DISCUSSION ON THE PROBLEMS OF RESINIFICATION

Freundlich⁷⁵ considers resins as gels of highly polymerized substances, the disperse phase consisting of a more highly polymerized form of material composing the continuous phase, and the plastic behaviour is parallel to that of glasses, and, moreover, is determined mainly by the viscosity of the continuous phase, the disperse phase being of secondary importance, i.e. they are two-phase colloids. For the development of plasticity with its variable coefficient of viscosity and, possibly, yield value, some affinity between solid and liquid is essential. The phenomenon of *thixotropy*, frequently met with in plastic masses and associated with loose packing of the parts, demands attractive forces between the latter of the van der Waals order. The above may be taken as the purely colloid aspect, which

correlates many phenomena successfully, especially those of comparatively simple structure; but structure is of great importance (cf. the properties and structure of bentonite and kaolinite) and is of equal importance in consideration of the properties of oil films and resins.

Thixotropy. This is the term used to describe the isothermal reversible gel-sol-gel transformation which can be induced by shaking or other mechanical means, and subsequent reversal. The reversal occupies an appreciable period of time. This is found in loosely packed systems of clay and bentonite, but not in closely packed ones such as quartz powder and water. A sufficiently great thickness of the liquid layer (300 Å.) is of importance for securing strong plasticity. The volume of the interstices, and therefore the volume of the liquid layers, increases when the packing is less close. The volume of sedimentation is small if the packing be close, and conversely. The observations of Osborne Reynolds on the close packing of sea sand, and the conclusions he drew, have a bearing on the problem of plasticity. With close packing plasticity will be poor and on deforming the mass it will become hard and brittle. Plastic masses must not be too closely packed, and they must have fairly thick layers of liquid around them. Summarizing, therefore, close packing and small volume of sedimentation signify no plasticity and no thixotropy. Loose packing and a large volume of sedimentation are found with plasticity and thixotropy.

The foregoing considerations hold generally if the particles are spherical: if they be plane, rather than spherical, streaks may appear on stirring. Particle size as well as shape influences plasticity. To form plastic masses the particle size should be between 0.3 and 3 μ , but if the particles are too small (colloidal size), the influence of the non-spherical shape, so valuable for the cohesion of the mass, decreases rapidly. The stronger Brownian movement of the smaller particles causes the whole mass to be less firm, and the interior surfaces between the two phases on which cohesion depends are smaller in area and irregular.

While too small a particle size is unfavourable to the development of plasticity, the maximum size must not exceed 10 μ . The amount of liquid which is responsible for the thickness of the fluid layers must bear a definite relationship to the amount of solid: this is impossible if the particles be too large. Moreover, if the particles be too large, they will tend to be too tightly packed and the interfacial area too small, both conditions detrimental to plasticity. Great hardness is also detrimental to the development of plasticity.

C. F. Goodeve⁷⁵ considers that non-Newtonian viscosity is composed of two independent parts, one Newtonian and the other thixotropic (*thixis*, touch, movement and *trepo*, to change), the latter being attributed to interference between particles and the formation of links. When stretched and broken, the links cause a series of impulses from a moving layer to a neighbouring layer, the amount of each impulse being inversely proportional to the rate

of shear, and the frequency (number/sec. of impulses) is proportional to the rate of shear; thus the product, the total force due to links, is independent of the rate of shear, a behaviour found with thixotropic substances. The theory is applicable to all colloid systems where there is interference between particles, and explains the thixotropy of foams and emulsions.

In a lecture on the polymerization of organic substances Freundlich discusses the polymerization of cellulose and rubber.⁷⁶ The X-ray investigation of cellulose fibres has shown that they are built up from small crystallites (crystalline micelles) of colloidal size, which are oriented parallel to the axis of the fibre. These crystallites or micelles consist of smaller units, the macromolecules. There is no reason to assume that the chains are strictly of equal length, i.e. of equal degree of polymerization. In the crystallites the chains are lying parallel to each other, presumably joined together by molecular forces (van der Waals forces). The oxygen bridges in the cellulose always seem to produce very rigid structure. The rigidity of the silicates, for instance, is generally attributed to oxygen bridges between the atoms of silicon. The macromolecules of cellulose are therefore, most likely, not very flexible but fairly rigid.

Rubber has a structure markedly different from that of cellulose. It does not show, in its natural state, the X-ray diagram of a crystalline substance, but on stretching the rubber sufficiently a spot diagram appears and the amorphous state diagram grows weaker.⁷⁷ Crude rubber consists mainly of macromolecules of different lengths. They are not rigid like the macromolecules of cellulose—the residues not being linked by oxygen bridges—but are flexible and extensible, most likely screw-shaped.⁷⁸ On stretching they are oriented, then extended; and thus groups of them, lying parallel to each other, unite to form a repeating unit and thus appear crystalline. In the styrene polymers (Chap. V), if the polymerization proceeds at room temperature, it takes a long time, but the product is highly polymerized; it is a 'eucolloid':⁷⁹ the X-ray diagram shows an amorphous state; on stretching, no such characteristic change is observed as in the case of rubber.⁸⁰ If styrene be polymerized at higher temperatures—up to 180°—using the catalytic action of tin tetrachloride or of ultra-violet light, similar glassy products are formed, but they are much more soluble in ether and benzene, giving solutions of a much lower viscosity; on the other hand, they do not swell at all or swell to a much lower degree. Freundlich considers that, although there is a great parallelism between the behaviour of rubber and drying-oils, one must be careful in correlating this behaviour too closely with that of resins. There is one very distinct property of resins, viz. the small tendency to form orientated particles. The particles of resin seem to be much more irregular in their whole structure and much less rigid. Not only are there long chains, but also side chains, which make the resins very different from other substances.

R. Houwink,⁸¹ from the study of the elastic and plastic properties of resins, makes the following proposals as to their structure:

- (1) Resins must be considered as Isogels (Wo. Ostwald). (An Isogel is a system where the dispersed particles have the same chemical composition as the continuous phase but differ in degree of polymerization or condensation. Gelatine is a heterogel.)
- (2) In most resins (natural and artificial) the micelles are globular in form (polystyrenes have elongated micelles).
- (3) The globular micelles are reversible or irreversible to heat action.

In the case of non-heat-hardening resins polymerization proceeds to a limited complexity and the micelles are linked together by secondary forces (not primary valencies); these resins may be compared with asphalts. By the heat-hardening resins primary valencies come into action, so that the whole gel is built of macromolecules, but before that stage is reached secondary forces hold the micelles together. In the case of resins with long micelles, an interweaving of the chains of primary valency linkage by secondary forces is to be imagined. Houwink considers that the above are in keeping with the elastic and plastic properties and also with the optical, Röntgen diagram, and viscosity properties.

Reference must be made to the work of Tammann,⁸² who has compared the temperatures at which resins change their physical properties, e.g. T_f is the temperature at which the drawing of wire from a molten resin is only just possible; on further cooling this possibility disappears; at the temperature T_g the mass becomes brittle, and plastic deformation becomes impossible. The transformation interval $T_f - T_g$ is characteristic for each kind of material, and for resins was found to be as follows:

	T_g in °C.	T_f in °C.	$T_f - T_g$ in °C.
Colophonium	29.5	52.5	23
Mastic	24.9	50.3	25
Shellac	30.5	56.5	26
Sandarac	36.1	63.5	27
Damar	39.1	68.7	29

The interval is small. Tammann calls all undercooled liquids 'glasses'; and the resins in the above table are named 'normal glasses', in contradistinction to polystyrene, polyindene, bakelite, and rubber. These latter are called 'abnormal glasses'. They show much higher ($T_f - T_g$) values: for polystyrene the difference was found to be 110°. In the 'normal glasses' it is assumed that all the molecules are freely rotating above T_f , whereas under T_g all the molecules are fixed, so the transformation interval is the transition between these two extremes.

The resins in the table given belong to the non-thermo-hardening

class and they may be assumed to be built up from rather small molecules for which the possibility of rotating freely can be accepted. The 'abnormal glasses' are thermo-hardening resins, and it is assumed that their molecules form large threads or are interlinked to form a network, so that no free rotation will be possible.

Modulus of Elasticity and Tensile Strength of Asphalts, Resins, and Glass compared with other Materials (Houwink)*

	Modulus of elasticity <i>E</i> in kg. mm. ⁻²		Tensile strength <i>F</i> in kg. mm. ⁻²		Elongation at proportional limit in per cent.	
	At 20° C.	At -195° C.	At 20° C.	At -195° C.	At 20° C.	At -195° C.
<i>Asphalts.</i>						
Asphalt† (various grades)	100-200	..	3-82 < 10 ²
<i>Resins</i>						
Colophonium	260	..	± 1 · 10 ²
Cresol formaldehyde:						
<i>A</i> stage	152	..	± 1 < 10 ²
Moulded 10 min./150° (<i>C</i> stage)	513	..	2.5
Moulded 60 min./150° (<i>C</i> stage)	500	803	3.3	3.8	0.6	0.5
Phenol formaldehyde:						
<i>A</i> stage	290	..	± 1 × 10 ²
Moulded 10 min./150° (<i>C</i> stage)	591	..	6.0
Moulded 60 min./150° (<i>C</i> stage)	595	1,050	6.7	7.8	1.1	0.7
Urea-formaldehyde‡ (cast) (<i>C</i> stage)	310-380	..	3
Aniline-formaldehyde§ (thermoplastic)	250-300	..	7
Polystyrene (mol wt. 48,000)	383	452	4.1	4.4	1.1	1.0
Shellac	135
Shellac (after 20 hrs. at 110°)	200
<i>Glass.</i>						
Technical glasses	4-8,000	..	3.5-8.5
<i>Other materials.</i>						
Cellulose derivatives¶ (acetobutyl, ethyl, xanthogen)	350-2,200	650-4,200	+ 20	10-12	± 10	20
Carbon steel (0.02 per cent. C)‖	20,000	..	29	..	0.05	..
Steel, heat treated (0.025 per cent. C.)	20,000	..	73	..	0.25	..
Steel (best spring)‡	20,000	..	197	..	0.77	..
Duralumin‡	8,000	..	36	..	0.17	..

* Experiments were carried out by means of the bending test, described, for instance, in E. G. Coker and L. N. G. Filon, *Photo-Elasticity*, Cambridge, 1931, p. 183. In this test specially the surface layers are stretched.

† E. Evans, *J. Inst. Petr. Techn.*, 1932, 18, 957.

‡ O. Manfred, *Le Caoutch. et la Gêtahe-Perlah*, 1927, 24, 13, 702.

§ K. Frey, *Helv. Chim. Acta*, 1935, 18, 491.

¶ J. Karger and E. Schmidt, *Z. techn. Physik*, 1923, 6, 124. These values were calculated from observations at room temperature after an ingenious correction for the plastic part of the deformation had been made. E. Valkö, *Melliand Textilber.*, 1932, 13, 461.

‖ S. Timoshenko and I. M. Lössels, *Festigkeitslehre*, 1928.

R. Houwink⁸⁵ discusses further the strength and modulus of elasticity of asphalts, resins, and glass. In the case of the asphalts, asphaltenes are assumed to be present in which the coherence is

probably effected by primary bonds, together with petrolenes bound to each other and to the asphaltenes by means of secondary bonds. According to Mark it is the behaviour of the petrolenes acting as a solvent for the asphaltenes which determines the elastic properties of asphalt. In the resins, as given before, the non-hardening resins are micelles and in the hardening resin *reactive spots* are supposed to be present on the surface of the micelles, which enable them to react with each other, passing from the isogel state through the *B* stage to the *C* stage in the phenol-formaldehyde resins. In glasses Houwink quotes Tammann (*loc. cit*) as indicating the role of secondary and primary bonds in glass formation. From the study of the modulus of elasticity and tensile strength of asphalts, resins, and glass, he concludes that the increase of the modulus of elasticity in stages *A*, *B*, and *C* of phenol-formaldehyde resins corresponds to replacement of secondary by primary bonds.

The low values for asphalts and non-hardening resins show the weakness of the secondary bonds.

Comparison of Experimental and Theoretical Values of Tensile Strength F^{86}

	<i>F</i> (observed)	<i>F</i> (calculated)
Phenol-formaldehyde resin (<i>C</i> stage) at liquid air temperature	7.8 kg. mm. ⁻²	4,300 kg. mm. ⁻²
Cresol-formaldehyde resin (<i>C</i> stage) at liquid air temperature	3.8 "	3,800 "
Glass normally	3.5 8.5 "	1,100§ "
Glass* under special conditions	350 630 "	
NaCl crystal† normally	0.6 "	200-400 "
NaCl crystal under special conditions	up to 160 "	

* A. A. Griffith, *Phil. Trans.*, 1921, **221** A, 163; *Proc. Int. Congress Appl. Mech. Delft*, 1924, p. 55.

† Compare A. Joffé, E. Orowan, and A. Smekal in *Proc. Internat. Conference on Physics*, Part II, London, 1934; A. Smekal in *Handb. der Physik*, **24**, 11, Berlin, 1933. A summary by W. G. Burgers and J. M. Burgers is found in the *First Report on Viscosity and Plasticity*, Roy. Academy of Sciences, Amsterdam, 1935.

§ This value was extrapolated from experimental figures. Calculations, based on atomic considerations, would lead to much higher values.

Houwink (*loc. cit.*) points out that high elasticity in polymerides seems possible only when primary linkings are present together with secondary linkings and perhaps a certain amount of fluid. For linear polymerides of sufficient chain length these conditions are always fulfilled with primary linkings in the chains and secondary linkings between the chains, and it seems reasonable to postulate that high elasticity is always possible for these polymerides. In the case of linear polymerides (chloroprene, vinyl chloride, isoprene) the resins meet the synthetic rubbers.

As an explanation of the low tensile properties of hardening resins

the idea of the 'Lockerstelle' of Smekal is introduced. Such 'Lockerstellen' would be represented in a macromolecule of a phenol-formaldehyde resin:

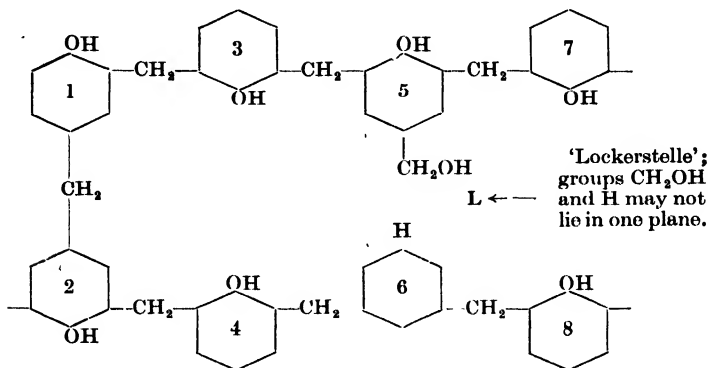


FIG. 52. A resin macromolecule in which a sponge-like structure ('Lockerstelle') is assumed

The occurrence of these spots may become less frequent as the molecule begins to increase in size. The steric conditions make the chance of the addition of a new single molecule at points 4, 5, 6, and 7 extremely small, as shown in the following figures:

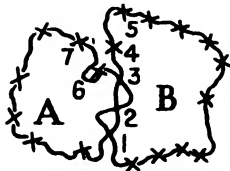


FIG. 53.

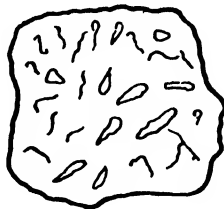


FIG. 54.

FIG. 53. Further formation of 'Lockerstellen' in a hardening resin. × represents chemically active spots; 1, 2, and 3 points of juncture; 4, 5, 6, and 7 spots where further growth is extremely improbable

FIG. 54. A macromolecule with 'Lockerstellen'

If the values calculated by de Boer⁸⁶ for the tensile strength on the assumption that only van der Waals forces are acting, the values are yet greater than the experimental, so that the presence of 'Lockerstellen' restricts even the action of these forces. The elasticity modulus for a phenol-formaldehyde resin is given by de Boer as:

<i>E</i> calculated for primary bonds	. 11,000 kg. mm. ⁻²
„ „ van der Waals forces	. ≥ 45 kg. mm. ⁻²

The experimental value of about 500 kg. mm.⁻² (cf. p. 488) may

point to the fact that the coherence in a resin molecule is effected partly by van der Waals forces. The discrepancy between the observed and calculated values of tensile strength is much greater and may be ascribed to the fact that the strength is determined only by the concentration of stresses at the most dangerous 'Lockerstellen', whereas the modulus of elasticity is given through the co-operation of the moduli of several bonds in the molecules. In the opinion of the writer of this chapter there would seem to be a connexion between the 'steric factor' and the Lockerstellen in polymerization. On the assumption of a chain mechanism, the size of the polymeric molecule is determined by the steric factor.

VAN DER WAALS FORCES

Van der Waals forces, or the general forces of cohesion, frequently referred to in this chapter, require special treatment. Investigations carried out during recent years have greatly added to our knowledge of the nature of these forces; in particular the mutual attractive forces between two or more electrically neutral and dipole atoms or molecules have in many cases become admissible of calculation. J. H. Boer⁸⁷ states that owing to the short period movement of the electrons in the atoms and molecules, which persists even at absolute zero, there exist in all atoms dipoles, which change continually in magnitude and direction. To explain the meaning of the term 'dipole' it is put forward that molecules exist in which the centres of gravity of the positive and negative charges do not coincide (e.g. H_2O , — \ddagger). These molecules therefore form a kind of permanent magnet, a *permanent dipole*, whose magnetic moment (dipole moment) is equal to the charge times the distance between the centres of the charges. Two such dipoles attract each other. At the same time dipoles may be induced in neutral molecules by an external electric field (induced dipoles). The inducing action may, for example, be that of an ion or of another dipole, whereby the ion or inducing dipole and the induced dipole will attract each other. The reciprocal energy between an induced dipole in an atom having a polarizability α and the inducing dipole with a moment μ situated in another atom at a distance R from the first is proportional to $\alpha\mu^2/R^6$. Therefore the binding energies due to van der Waals forces will vary in the inverse proportion to R^6 , or

$$E = -\frac{C}{R^6},$$

where E = reciprocal binding energy,

C = constant (calculated from the approximation formula of F. London, *Z. Physik*, 1930, **63**, 245).

The attractive forces will be inversely proportional to R^7 .

The magnitude of the van der Waals forces is in the first instance independent of the direction. The value of the reciprocal energy of

a given atom with respect to a large number of other atoms can be obtained by simply adding the reciprocal energies with respect to each of these other atoms individually. Because of its great dependence on distance the magnitude of the reciprocal energy will be determined chiefly by those atoms which can make the closest approach to the atom under discussion. Because of this circumstance, two molecules, which attract each other by means of van der Waals forces, will always have a tendency to orientate themselves into such a position that the largest possible number of atoms are in contact with each other. Thus hydrocarbon chains will show a tendency to be orientated so that their long axes are parallel and two benzene molecules will prefer to lie with their flat sides together. The reader must be referred to the mathematical development of the application of the influence of van der Waals forces on tensile strength of common salt and artificial resins of the phenol-formaldehyde type and *m*-cresol-formaldehyde type. In the case of the latter it may be assumed that the whole is built up of relatively large regions, within which the constituents are bound by primary bonds and which are themselves fastened to each other by means of van der Waals forces. De Boer states that if such an artificial resin be completely polymerized throughout its whole mass and all the C-C linkages possible are actually formed, the theoretical tensile strength may be calculated to be about 4,000 kg./mm.² if (irregular) 'blocks' are assumed in this case also, and if these blocks are assumed to cohere only by means of van der Waals forces, then the theoretical value is about 35 kg./mm.

The experimental value is about 7.8 kg./mm., so that here there is an influence of a 'notch' effect arising from defects in the lattice and not a regular secondary structure. On the other hand, in the case of well-orientated cellulose derivatives, a nearer order of magnitude for the tensile strength may be obtained by theoretical conclusions. The fact that with many fibres, even in a well orientated state, very much lower values are found is ascribed to the presence of 'Lockerstellen' between the crystallites. This brief abstract of de Boer's paper will show what progress has been made in the application of van der Waals forces to the problems of polymerization, condensation, and resinification. With respect to particles of colloidal size it has been calculated that for large ionized particles the minimum of potential energy may lie at a distance which is of the same order of magnitude as the radii of the particles. At this distance the attraction might be strong enough to maintain a coherence between particles which otherwise would be separated by Brownian movement. The secondary bonds are of importance in colloid systems, e.g. in *solvation* (the glueing of a liquid to a solid substance), *association* (the joining of molecules to form larger groups, e.g. $n\text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})_n$), and the formation of *swarms* (very loose groups in which cohesion is disturbed by the process of flowing (thixotropy)). In the case of secondary bonds the molecular cohesion is greater for a polar group (e.g. OH or CO) than for a non-polar (e.g. CH₃). The difference in

energy between primary and secondary bonds is manifested in resistance to mechanical deformation; the lubrication action of graphite may be traced to the ease with which the secondary bonds between the layer lattices may be broken. For further comparison between primary and secondary bonds reference may be made to Houwink's *Elasticity, Plasticity and Structure of Matter*, Cambridge, 1937.

CRITICAL SUMMARY ON POLYMERS AND CONDENSATION REACTIONS

A valuable critical summary on Polymers and Condensation Reactions was presented at the 1935 Conference of the Faraday Society at Cambridge by E. K. Rideal, and a full statement is advisable.⁸⁸ Three types of structure resulting from polymerization or condensation may be recognized. The first and simplest is that of linear growth, which may be designated as the A_n or $[AB]_n$ type. The estimation of the mean chain-lengths may be obtained by chemical methods or physical methods, e.g. optical extinction coefficient, magnetic susceptibility, or dipole moment. It is a matter still for speculation whether the natural growth of a linear polymer or condensation reaction chain is spiroform (cf. Freundlich). If the van der Waals forces of lateral adhesion along the chains be great enough, the formation of a spiral is rendered more probable. The nature of the chain material as well as that of the solvent must be important factors in the form of the resulting chain.

The second type of structural unit is to be found in the large ring. It is possible that such closed systems in the form of parallel elongated threads, imitating the linear polymer in their general form, but essentially bifilar, are far more common than is generally suspected.

The third and most complex type of structural unit is the cross-linked polymer or condensation product. The simplest example is to be found in the hydrolytic products of silicon esters (cf. p. 455).

KINETICS OF POLYMERIZATION PROCESSES

In the kinetics of the A_n type of polymer the growth of the macromolecule can be shown to be dependent on one or two possible processes. Dimers may be formed with subsequent union with one another, or the polymer may grow by addition of the monomer to the growing chain of the polymer. This last aspect presents several analogies with the chain reactions of classical kinetics. Four factors have to be considered, viz. chain initiation, chain prolongation, chain branching, and chain termination. Moreover, three energies of activation are involved: E_1 for the initiation, E_2 for the prolongation, and E_3 for the branching of the chain. For reactions in the gaseous state or in solvents the rapid growth of chain is frequently more than compensated for by the *steric* factor. It is clear that

collision of a monomeric molecule with the polymer with sufficient energy of activation is not sufficient condition for reaction; the monomer must collide within an area on the ever-growing polymer, which area remains constant regardless of the size of the polymer. It is possible from the data available on the rates of addition of bromine to olefines and similar reactions that the active target area on the growing polymer is increasingly shielded as the polymer grows, and it would seem possible that longer chains could be formed if the polymer were suitably orientated for reaction or with a suitable steric factor. For systems capable of forming cross-linkages, e.g. silicon esters or certain of the glyptals, the relative magnitudes of E_3 (the energy of activation for cross-linkage equivalent to gas kinetic branching) and of E_2 (the energy for linear propagation) are important. In the case of silicon esters they do not appear to differ to any considerable extent, and hence cross-linkage is difficult to avoid; but in the glyptals the reactivity of α - and β -hydroxy groups differs sufficiently to permit of a relatively rapid linear growth at low temperatures with a small velocity of cross-linkage, which latter grows relatively to that of the linear propagation on elevation of the temperature yielding a heat-convertible resin. The same state of affairs may be possible in the substituted phenol condensation product. *Para*-substitution limits the polymer to the $[AB]_n$ type with occasional and difficult *meta*-cross-linkage.

Little attention has been paid to the mechanism by which a growing chain undergoes termination. Rideal put forward the following provisional classification:

(a) The chain may grow indefinitely, but with an increasing steric factor, the exponential fall in the velocity coefficient with increase in chain-length means virtual cessation of growth after relatively short chains have been formed, e.g. the drying-oils. In drying-oils a steric factor appears to be important and the polymer must be regarded as spherical rather than thread-like (Morrell, loc. cit.).

(b) The chain may cease growing or disintegrate on account of a special type of collision with a molecule of monomer involving a different energy of activation and a different number of squared terms from those involved in chain growth.

(c) The chain may require a positive catalyst for initiation and a negative catalyst for stopping. In some cases the initiator and inhibitor may be identical; the apparent reaction velocity thus goes through a well-defined maximum on progressive addition of catalyst, and the varying and falling apparent energy of activation is observed.

(d) The probability of the reversion of the active group of the growing polymer to the inactive form may be a function of the chain-length, or, if the activity of the end group be determined by an energy of activation, rather than by its existence in a tautomeric form, the probability of this energy being dissipated increases with the size of the polymer, i.e. with the number of squared terms. This

view, which has been advanced on many occasions, does not appear very plausible for long-chain polymers.

(e) The length of the finished polymer may be regarded as the result of an equilibrium between polymerization and depolymerization. The thermal degradation of substances such as polystyrenes and the mechanical degradation of rubber-like substances, e.g. polyprene chains cross-linked at intervals by oxygen or sulphur are well-known examples of such apparent reversion. Cf. also p. 452 of this chapter.

In discussing swelling and dispersion Rideal states that in dispersive solvents the whole polymer may not be dispersed, but a solution containing macromolecules and macromolecular assemblages in the form of micelles may be formed. With cross-linked polymers a great variety of changes may ensue. The material might consist of a system of micellar units each containing a number of macromolecules linked together by primary valencies and each micelle discrete and separated from each other by, as it were, a shield of terminal groups (cf. Wornum, p. 482), or the whole block may be considered as a large macromolecule containing *Lockerstellen* (see Houwink, p. 490) or lines or planes of weakness representing the terminal groups which have not reacted. A large *steric* factor in the growth of a cross-linked polymer would evidently favour the former and a small steric factor the latter form of growth. The idea of steric factor implies that as the polymer grows, the chance that a fresh molecule shall hit it in the right way or at the right place to be incorporated in the big molecule is decreased. This naturally results in few molecules growing beyond a certain mean size in any particular case. Heat-polymerized linseed oil and silica gel may be considered as representative of these two types. The number and nature of cross-linkages affects the dispersability and also the swelling properties; increasing the number of cross-linkages in rubbers by oxygen or sulphur renders it less elastic and more brittle. When polar or binary mixtures of polar and non-polar solvents are employed, it is clear that the conditions in the swollen system are complex, because the macromolecules form a repeating system of groups around which the molecules are selectively and directively orientated at low temperatures.

Imbibition and swelling of the solid is associated with the formation of micelles, whereas cross-linked polymers, e.g. silica, vulcanized rubber, or phenol-formaldehyde resins, do not swell or disperse in solvents. In the general study of swelling three types may be recognized: the intermicellar (floculate systems), the intramicellar (micellar systems), and the permutoid (molecular systems). In the intermicellar swelling, the liquid is absorbed only at the surface of the micelles with the formation of lysospheres. In the intramicellar type the micelles are penetrated, the liquid forcing apart the discrete structure units, which build the micelle. In the permutoid or highly disperse swelling the liquid is bound to the disperse-phase molecule by molecular combining forces.

Swelling arises from an attraction between the liquid and the

swelling substance by the valence forces operating in the flocculate or micellar formation. If this attraction lead to neutralization of these forces, dispersion will result; if not, the swelling will lead to an increase in particle size of the disperse phase. One molecule of cane sugar carries with it six molecules of water during diffusion in the liquid. Whether such swelling will lead to ultimate dispersion will depend on the rate of such dispersion being greater than the rate of coagulation under the conditions considered.

Staudinger has prepared a series of products from polystyrene which may be considered as thread-like macromolecules which will go into true solution in organic solvents, the process of solution being preceded by solvent imbibition and swelling. If a small quantity of *p*-divinyl benzene be added before polymerization, then when the chains are formed molecules of this material are incorporated in the growing chain and cross-linkages come into existence by the formation of divinyl benzene bridges. Such a cross-linked system is no longer dispersible in solvents, although, if not too many cross-linkages are formed, the material is capable of swelling. If the ratio of styrene to divinyl benzene be as high as 50,000 to 1 the product is highly extensible, but insoluble, whilst if it be as low as 1,000 to 1 the product shows hardly any sign of swelling at all. Rideal states that it is clear that the properties of the polymers and condensation products may be altered to an extraordinary extent by the addition of suitable materials, even in sub-analytical amounts.

In discussing the mechanical properties of polymers and condensation products in relationship to their constitution, Rideal pointed out that the maximum force exerted to separate two carbon atoms in a chain must be of the order of 5×10^{-4} dynes, which gives the tensile strength of 500 kg./mm.², the actual value of rupture being about 5 kg./mm.² for phenol condensation products and 80 kg./mm.² for orientated rubber. If separation occurred across a plane where van der Waals forces alone were operative, the calculated value would be of the order of 20 kg./mm.² The discrepancy may be partly resolved in two ways: the actual rupture may consist in the process of tearing at a 'Lockerstelle' (cf. p. 490) or the apparent weakness may in some cases have a chemical origin, as in the case of cross-linkages of the isoprene type, where polymers by means of oxygen or sulphur double bonds are involved. Several problems in connexion with the elastic properties of macromolecular aggregates are referred to.

On progressive growth of linear macromolecules van der Waals forces increase and the true molecular dispersion in any solvent becomes more difficult with increased tendency for micelle formation. If chemical methods be employed based on the analyses of the end groups it is important to ensure that no cross-linkage can occur to form relatively unstable systems. With viscosity methods the solution must be sufficiently dilute to disperse all micelles to single macromolecules.

In a recent summary on the correlation of properties of macromolecule substances with their structure and mode of synthesis⁶⁰ in-

stanced by (a) cellulose and its derivatives, (b) vinyl polymers, it was considered impossible in either case to account quantitatively for the relatively poor mechanical properties, e.g. tensile strength and modulus of elasticity as compared with the values calculated on the assumption that these properties are wholly dependent on the nature of the primary valencies existing in the macromolecules. The forces determining the physical properties must be largely of an intermolecular variety of a magnitude which it is very difficult to compute. In the consideration of toughness and molecular architecture, toughness is a complicated function of impact resistance, tensile strength, extensibility, Young's modulus, and bending strength. The Schopper curves obtained by plotting the load on a material as a function of the percentage elongation, in the case of tough plastics such as nitrocellulose, cellulose acetate, and ethyl cellulose, suitably plasticized, show rapid rise and flattening out over a considerable elongation, especially in the case of cellulose triacetate and nitrate. For the exhibition of high extensibility, however, all the molecules must be plasticized, but experiments with other celluloses have shown that a plasticizer is not really necessary if, e.g., ethyl groups replace the hydrogen atoms of the hydroxyl groups. Unfortunately the tensile strength of ethyl cellulose is inferior to that of nitrocellulose. Vinyl compounds do not show high extensibility, although vinyl chloride is regarded as being very tough. The great extensibility of cellulose derivatives can be simulated if appropriate side-chains are added to the molecule as in polyvinylbutal, but at expense of a decrease in tensile strength. The addition of plasticizers does not improve matters, as with cellulose, because this material loses its resistance to deformation and becomes rubber-like in character. Progress is hampered in this field by ignorance of molecular weights and molecular size distribution on the majority of these polymers. Staudinger's viscosity method has been largely used for linear molecules, but the values obtained do not agree with those calculated from end-group determination (p. 71), nor by osmotic pressure and Svedberg's ultracentrifuge methods.⁹⁰

By Staudinger's method the viscosity increase is proportional to the molecular weight, but hydrodynamics indicate that it is proportional to the square of the molecular weight. If one assumes that the dissolved particles be not spheres or stiff rods, but flexible threads, the experimental findings and the theoretical equations harmonize in a manner, which shows that the idea of long flexible chains rolled or wound up to a more or less cluster unit is the right way out of the dilemma.⁹¹ With increasing molecular weight the solvation of the substance increases and in the case of styrene deviation from the spherical shape assumes higher values. H. Mark and R. Simha⁹² conclude that if account be taken of the fact that it is very difficult to get trustworthy quantitative information on size, shape, and solvation in the region of high molecular weights, it will certainly be admitted that viscosity methods provide a very valuable means of obtaining quantitative information on the molecular structure of such

materials. The influence of the solvent is shown in acetone with 20 per cent. cellulose which is a fluid and also mobile, but in dimethyl phthalate of the same concentration the system yields a stiff gel. It seems to be a general rule that properties, e.g. tensile strength and Young's modulus, increase to a rough maximum with increase in molecular weight. The absolute value of these quantities depends on the nature of the side groups. The groups exhibiting relatively small interactions, e.g. phenyl, lead to weakness, whilst hydroxyl, formal and acetal groups, and chlorine atoms yield stronger polymers, even although the length of the carbon chain is identical in both cases. Comparison with the conclusions drawn by Mark on p. 417 are of interest. According to Couzens, Hetherington, and Turner actual molecular size, while it influences the strength of plastics of the same kind over a certain range of size, is of little use for comparison of plastics of different chemical structure. The above conclusions have had their effect in improving natural resins by systematic methods. In the case of shellac (pentahydroxy-mono-basic acid, mol. wt. 1,000) this resin is of no use as a plastic, but it may be modified to give useful products. On heating it is polymerized to linear molecules of higher molecular weight due to interaction between (OH) and carboxyl groups, because esterification of either of them prevents polymerization. By further heat treatment shellac may be made insoluble owing to cross linking caused by the presence of (OH) groups in the monomer. By reaction with ethylene glycol the activity of the hydroxyl group is cut down and cross-linkage impeded, with the result that much longer linear molecules may be formed with molecular weights up to 24,000. The polymerized lac is then a tough flexible rubber-like substance. Inter-polymerization of shellac with naturally occurring unsaturated resins gives rise to a product similar to drying-oils used in paints. Further, such composite molecules may be induced to react with formaldehyde to give complex linked molecules of desirable film-forming properties. The work on shellac is the product of the Lac Research Institute under the leadership of Dr. Bhattacharya. It is an interesting example of application of resin properties and shows that the recent investigation of the problems of resinification is giving valuable technical results.

Reference must be made to Bhattacharya's views on the structure and polymerization of natural resins.⁹³ According to him the degree of polymerization of natural resins is low and it is doubtful if the primary valencies be active to any degree, whereas the secondary valencies and van der Waals forces are potent, so that copal may be rendered soluble in solvents by a mastication process.⁹⁴ In the case of shellac the resin becomes insoluble at 120–135° to the extent of 75 per cent., due to the formation of intermolecular esters and ethers.

SUMMARY

It is impossible with the great variety and diversity of opinions to reach definite conclusions as to the causes of polymerization and

resinification. It must be admitted that the prospects of general agreement are brighter, but much more work is necessary. An attempt has been made to state the views of the chief investigators in the field and to leave the reader to form his own opinion. According to Sterne 'The truest respect you can pay to the reader's understanding is to leave him something to imagine, in his turn, as well as yourself.' Any summary by the writer of this chapter must be inadequate, and it is with great diffidence that he draws attention to the following aspects. Comparison between Herzog and Kreidl's resinophore groups and Staudinger's chain theories shows that preference has been given to the latter in any explanation of the causes of resinification. The great difficulty is essentially the complexity of many of the resinous systems; e.g. Pollak and Riesenfeld put forward that the resinous character is not the result of specific molecular size, but may be attributed to the presence of a number of isomeric compounds such as are found in the phenol-formaldehyde condensations. From Carothers's work the resinous properties are conditioned by the length of the chain and by the character of the components.

The value of Kienle's postulates has been shown in the study of a number of resin systems. Freundlich (p. 493) has referred to forces stronger than van der Waals's. Reversible and irreversible micelles have also been considered (Wornum, p. 482).

The polymerization chain mechanism of Chalmers involves the action of primary valencies. The influence of the addition of small quantities of *p*-divinyl-benzene on the physical properties of the polystyrenes is of great interest (p. 496), indicating that in the case of proteins of highly polymeric structure a minute change of composition affects greatly their physical properties (Staudinger). The work of Pollak and Riesenfeld (p. 459) on the correlation of dielectric properties and the chemical composition of bakelite resins is worthy of careful consideration.

The results of Houwink's studies of the elastic and plastic properties with the application of the idea of Smekal's Lockerstellen are very striking. The consideration that a steric factor conditions the structure of polymers must not be neglected in resinification problems.

The view of R. Houwink (p. 463) of the importance of secondary forces to give micelles, built up by such forces and forming macromolecules when the primary valencies come into action, is an additional aspect that is worthy of careful consideration. The secondary forces, stronger than those of van der Waals, are considered by some to be of the nature of dipole moments; this would allow of consideration of the chemical constitution of the gelating substance. The difficulty seems to be to evaluate these forces (cf. de Boer, p. 491). If such an evaluation could be achieved, progress in the causes of resinification would be advanced. The writer has recently examined drying-oil systems yielding 'oxyns' in which two forms could be identified, one in which secondary forces, most probably of

a dipole character, produce a gel retaining the active oxyn groups. In the other the primary valencies had come into action and produced chain molecules containing less active groups. The gels had originally the same chemical composition, but were produced in different media (non-polar and polar). The first mentioned gels differed in elastic properties, the former being tough and the latter brittle. In another drying-oil system the marked increase in viscosity could be shown to be due to the action of secondary forces, whereas at a higher temperature gelation ensued and it could be demonstrated that the primary valencies had now come into action; the gelled system was no longer dispersible by solvent media. It seems that definite progress will be made by a study of systems in which these secondary forces can act. Many of the synthetic resin systems are exceedingly complicated, so that the investigation of such forces seems at present fraught with great difficulty.

Comparatively little is known of the activity of dipole units in chemical systems. Reference has been made in former pages under bakelite and urea resins to show that polar hydroxyl and unsymmetrical CH_2 groups may play a part, but the determination of the dipole moment of different phases of the resin has not been undertaken. In the writer's opinion a strong dipole moment either of an unsymmetrical double linkage or of a marked polar group will indicate a tendency to an association to produce micelles which, following the view of Houwink, may pass into a macromolecule in which the primary valencies are the attractive forces. It may be assumed that such dipole forces may bring the molecules within a distance of 3.5 Å. and primary valencies establish contact at a distance of 1.5 Å. between the units. The final arrangement of the resin unit may be looked upon as a chain molecule in 1 dimension with other chain molecules in 3 dimensions forming an aggregate of macromolecules, together with micelles composed of aggregates, which may be chain molecules or *not*, held together by polar forces.

Since Rideal's summary of the knowledge of polymerized systems definite progress has been made. The results of the work of Melville and others, described at length in the previous chapter, bring the theoretical aspect into closer connexion with the problems of everyday requirements. The part played by free radicals has been extended and the function of catalysts, together with the conditions of chain formation and chain termination, are better understood. The principles of Kienle's postulates still hold, although further modifications are to be expected. The activity of dipoles in gel and in resin formation requires further investigation and the functions of macromolecules (Staudinger) *v.* micelles (Mark) remain still under discussion.

Although the macromolecule aspect has made progress with the help of definite experimental confirmation, the micellar aspect, lacking similar experimental support, remains yet an important factor.

APPENDIX I

X-RAY EXAMINATION OF NATURAL AND SYNTHETIC RESINS

No definite or generally accepted conclusions can be drawn from the X-ray examination of these amorphous solid substances. In the Debye-Scherrer pattern two diffuse rings are shown characteristic of the amorphous state, although in the case of several soft natural resins a crystalline structure may be indicated. In Meyer and Mark's *Der*



FIG. 55. Phenol-formaldehyde resin

(a) Low condensation stage

(b) High condensation stage

FIG. 56. *m*-Cresol-formaldehyde resin

(a) Low condensation stage

(b) High condensation stage

(R. Houwink⁹⁶)

Aufbau der hochpolymeren organischen Naturstoffe, p. 184, diagrams of stretched and unstretched rubber sheets are shown. On p. 263 of H. Staudinger's *Die hochmolekularen organischen Verbindungen* are shown Debye-Scherrer patterns of polyoxymethylene films, and on p. 295 the corresponding pattern of polypropylene-oxides.

The subject has been reviewed by G. F. Beal, H. V. Anderson, and J. S. Long,⁹⁵ and by R. Houwink.⁹⁶ Morgan⁹⁷ states that X-ray study of ready-formed synthetic resins yields little definite information because only ill-defined halves are perceptible and accurate deductions are difficult. On the other hand, C. S. Fuller⁹⁷ concludes that X-ray investigation of

polyesters shows that their rubber-like plasticity is associated with their amorphous component. Beal and his collaborators examined X-ray patterns of the series of natural and synthetic resins. In general the patterns consisted of broad halos or rings surrounding the central image produced by the undeviated X-ray beam. They varied in diameter, width, intensity, and number according to the resin. The details of the mode of examination will be found in the above paper.

The X-ray patterns of a series of natural fossil resins have been studied by Mahadevan.⁹⁸ He found that the softer resins give larger spacing, and with increasing hardness the intermolecular distances became smaller. In the case of the natural resins, Zanzibar, Congo, Manila, and Damar, two strong halos of about equal intensity were observed in Zanzibar and Damar; with Congo the inner halo was slightly broader and more intense than the outer. Vaidyanathan⁹⁹ studied the monocyclic and bicyclic-hydrocarbon terpenes, many of which have been identified with the natural resins. He concluded that the diagrams indicated that resins (natural) have a structure similar to that of the terpenes.

In the coumarone-indene resins Beal and his collaborators concluded that the molecules are first polymerized into groups or clusters having the thickness of a single molecule. All the molecules of a single cluster must therefore be in the same plane. As the polymerization proceeds, these clusters begin to line up in parallel layers, separated by a distance equal to the thickness of a coumarone molecule. The layers are evidently held together by some type of association rather than by primary valency forces.¹⁰⁰

Houwink¹⁰¹ is, like Morgan, not so optimistic on the results of the X-ray examinations. The diameter of the rings are not always equal for different varieties of the phenol- and cresol-formaldehyde resins, which may indicate different sizes of the basic molecule. Progressive polymerization shows no appreciable alteration in the diagram, and indicates that no change in the distance of the basic molecules can be detected. In none of the amorphous resins could signs of orientation be produced, so that anisodiametric structures of the molecules could not be proved; nevertheless, the possibility of orientation must not be excluded from the results of X-ray examination. In the case of natural resins which contain crystalline particles it is possible to indicate an orientation. He admits that in the coumarone-indene resins examined by Beal and collaborators there were some changes in the X-ray diagram on polymerization. He quotes Trillat's conclusions,¹⁰² that in the cresol-formaldehyde resins the elementary cells are very small, consisting of a few C-atom groups, and that polymerization is accompanied by a 'reserrement des groupes diffractants', which connects with physical changes noticed in bakelite. He gives diagrams to show that phenol and cresol rings differ only slightly, and speculations respecting the size differences of elementary cells are possible. In the examination of drawn and pressed filaments of bakelite resins Houwink states that no possible orientation in the case of *ortho*- and *para*-cresol resins could be observed. The results from the examination of urea- and thio-urea-formaldehyde show that they are amorphous substances with X-ray diagrams similar to those of the phenol-formaldehyde type.

N. J. L. Megson and W. A. Wood¹⁰³ have studied the X-ray appearances which precede the formation of a resin; on heating cryst. *p*-cresol monoalcohol the photographs show the formation of a new intermediate product (m.p. 99-100°) and the spectrum of the final resin shows

unmistakably the same characteristics, from which it appears that the resin possesses a crystal structure with a molecular arrangement similar to that of the intermediate compound.

J. R. Katz communicates an X-ray observation on polyoxymethylene diacetate (Staudinger), which indicates that in the above crystalline substance the molecules must be in the form of long straight rods. He points out that few crystalline synthetic polymers have been sufficiently investigated and recommends as promising fields the group of polyesters synthesized by Carothers and his collaborators.¹⁰⁶ In the analyses of amorphous patterns of synthetic polymers there is great uncertainty in the conclusions. In the low-boiling liquid butadienes the amorphous patterns are the same as the thermal polymers made therefrom (butadiene, $\text{CH}_2 : \text{CH} \cdot \text{CH} : \text{CH}_2$, isoprene, $\text{CH}_2 : \text{CH} \cdot \text{C}(\text{CH}_3) : \text{CH}_2$, and β -dimethyl butadiene, $\text{CH}_2 : \text{C}(\text{CH}_3) \cdot \text{C}(\text{CH}_3) : \text{CH}_2$); nevertheless, the amorphous pattern may be entirely different in polymerized and non-polymerized forms, as in the sodium polymers of butadiene or vinyl acetate or methyl acrylate, and a ring of smaller diameter is introduced (polymerization ring) in the case of styrene, coumarone, and polyindene polymers. In describing the X-ray diagrams of polyvinyl alcohol, thiokol, polychloroprene, methyl rubber, and isoprene rubbers, he concludes that polychloroprene (Duprene) is a derivative of gutta-percha, and not of rubber, and that the synthesis of natural rubber from isoprene has not yet been made. It is possible that the rubber molecule on stretching is converted from a coiled-up molecule into a straight one.

Polysobutylene when stretched passes from the amorphous X-ray diagram to a fibre pattern analogous to natural rubber. R. Brill and Halle concluded that the stretched molecules were probably helical and not planar zig-zag in shape (cf. p. 325). C. S. Fuller, C. J. French, and N. R. Pape¹⁰⁶ find that the chain molecules in the crystalline region assume a coiled form and possess 1:3 disposition of the methyl groups. The X-ray results give a chain configuration in isobutylene as that of a helix in which successive methyl group pairs pack together in a staggered arrangement. This requires successive partial rotation of the methyl group pairs at an angle of 45° around the molecular axis with coincidence after eight rotations. This arrangement is identical with that proposed by Meyer and Mark for natural rubber, but later work has modified this in favour of a less symmetrical group.

Butadiene gives a good X-ray spectrum, whereas isoprene forms a glossy mass and shows only liquid rings and chloroprene 3 lines and 2 diffuse rings.¹⁰⁷

P. A. Thiessen and W. Kirsch¹⁰⁸ show that for rubber under pressure (10-25 atm.) for each temperature there is definite pressure at which crystallization will occur spontaneously. Rubber hydrochloride has a crystal X-ray structure (unlike balata hydrochloride) indicating some cyclization of the rubber. Above 90° the rubber hydrochloride becomes elastic and when racked shows a typical fibre diagram.¹⁰⁹ X-ray diagrams show some definite relationship between the structure of rubber¹¹⁰ at low temperatures and the structure of polystyrene at ordinary temperatures.¹¹¹

Drying oils. In contrast to the results obtained from varnish resins, which have been criticized by Houwink, the examination of the hydrocarbon polymer chain resins has yielded valuable results. Respecting the molecular structure of drying-oils and their oxyns reference may be made to a communication by A. V. Blom described briefly below:

The molecular structure of a drying-oil and a diene polymeride as deduced from X-ray analysis is shown in Figs. 57 and 58 below.¹¹²

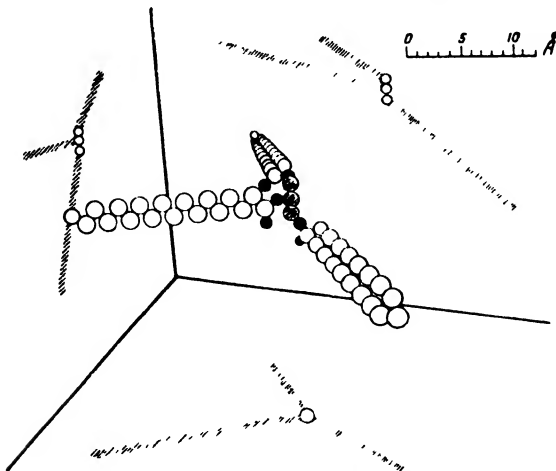


FIG. 57. Model of a Drying-oil Molecule

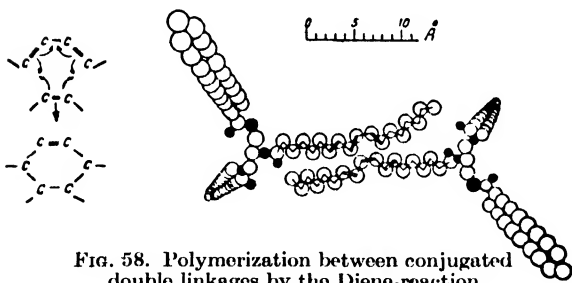


FIG. 58. Polymerization between conjugated double linkages by the Diene-reaction

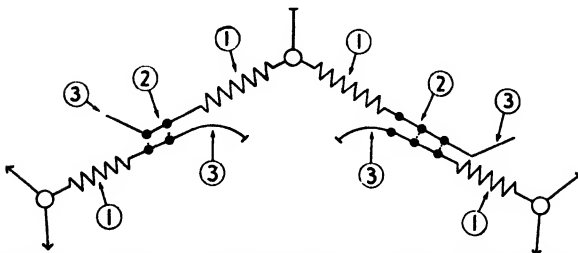


FIG. 59. Model of an Oxyn. (1) inactive section; (2) active section; (3) chain end

From this it will be seen that upon an axis of 3.1 \AA length are attached three chains of unsaturated acids of about 25 \AA length, which can rotate about the short axis. Measuring from the glycerol axis, no reactive groups

((CH₂)—COO^{*}) are present within a distance of 11 Å, so that this part of the molecule may be taken as common in all oil films. External to this nucleus the reactive double bonds are capable of forming peroxides and polymericides. Fig. 59 illustrates the structure of an *oxyn*, where the chains are bound by the polar peroxide groupings.

APPENDIX II

OPTICAL PROPERTIES OF RESINS IN RELATION TO MOLECULAR STRUCTURE

Densities and refractive indices. Reference to the following table will show the variation of these characteristics.

The density may be determined by a flotation method.

Refractive index, according to Bradley (*loc. cit.*), may be determined by the Becke or oblique illumination methods.¹¹³ The Abbé type of refractometer is not suitable, because most resins melt between 70° and 200°. At present there is no suitable method published, and the need of simplification of Bradley's procedure is desirable.

Densities and Refractive Indices at 18° C.*¹¹⁴

<i>Natural Resins</i>	<i>Density</i>	<i>Refractive Index</i>	<i>Specific Refraction, K</i>	<i>Synthetic Resins</i>	<i>Density</i>	<i>Refractive Index</i>	<i>Specific Refraction, K</i>
Shellac (orange)	1 152	1 516	0 282	Glycerol phthalate	1 389	1 575	0 238
Rosin (M)	1 069	1 525	0 228	Ethylene-glycol phthalate	1 352	1 570	0 243
Congo Copal (pale)	1 066	1 540	0 2990	Penta-erythritol phthalate	1 390	1 584	0 242
Canada Balsam	1 00	1 530	0 309	Coumarone-indene resin	1 140	1 645	0 318
				Vinyl acetate polymer	1 15	1 473	0 244
Manila Copal (hard)	1 072	1 544	0.295	Com'l toluene-sulphonamide resin	1 35	1 596	0 252
Manila Ester	1 090	1 506	0 273	Com'l urea-thio-urea-formaldehyde resin	1 477	1 660	0 250
Kauri (grade 303)	1 043	1 540	0 305	Cresylic acid-formaldehyde	1 12-1 2	1 57-1 65	0 293-0 300
Damar No. 1, Singapore	1 062	1 515	0 284	Condensation product (Resol)	1-15-1 3	1 54-1 70	0 260-0 297
Pontianac	1 068	1 545	0 296	Phenol condensation product (Resol)	1-050-1-07	1 610-1-67	0 330
Gum Sandarac	1 078	1 545	0 293	Polystyrene	1-713	1 703	0 226
Gum Mastie	1 070	1 536	0 291	Chlorinated diphenyl resin	1 207	1 544	0 281
Rosin Ester	1 095	1 496	0-267	Cyclohexanone-formaldehyde resin	1-2	1-52	0 253
Congo (fused to 30 per cent. loss in weight)	1-050	1 545	0 311	Benzyl cellulose	1-14	1-47	..
Congo Ester	1 076	1 506	0 276	Ethyl cellulose			

A resin manufactured by Stafford Allen for the Scientific Instrument Research Association has a very high refractive index (1.8).

* The density determinations of the synthetic resins were made both by the flotation and water-displacement methods as referred to water at 20°. The refractive indices of the synthetic resins were determined by the Becke method, using indirect illumination from a 75-watt, 110-volt Mazda bulb and a total magnification of 150 diameters (Bradley).

<i>Inorganic glasses</i>	<i>Density</i>	<i>Refractive Index, n_D</i>	<i>Synthetic resins</i>	<i>Density</i>	<i>Refractive Index, n_D</i>
Sheet window glass	2.50	1.51	Cellulose acetate	1.27-1.37	1.47-1.50
Soft soda glass	2.45	1.48	Cellulose nitrate	1.35-1.60	1.50
Lead flint glass	4.0	1.8	Polymethyl methacrylate	1.18	1.50-1.52
Borosilicate glass (Pyrex)	2.25	1.47	Polyisopropenyl methyl ketone	1.11-1.15	1.52
Fused silica (Vitreosil)	2.21	1.45	Polyvinyl chloride acetate	1.34-1.36	1.53
			Cast transparent phenol formaldehyde	1.27-1.32	1.5-1.7

The refractive index (n) is better expressed as the specific refraction K , e.g.:

$$K = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$$

K remains constant when the state of aggregation, and therefore the density (d), are changing. For a mixture of two materials A and B with specific refractions K_A and K_B respectively the equation given holds:

$$(p_a + p_b)K = p_a K_A + p_b K_B,$$

where p_a and p_b are the mixing ratios. If, after mixing, a different value of K is found, it may be concluded that reaction has taken place, and when such a reaction is proceeding the alteration of K can be used for following the reaction process.

Comparison of the values of n and K with those of the synthetic resins shows that the latter are higher, with the exception of the vinyl resins, but the values of K , as shown in the previous table, are not markedly different. There is little known of the alteration of the refraction of natural resins when subjected heat to treatment. Houwink¹¹⁵ has observed a slight change in Manila copal and shellac when heated for 100 hours at 110°. Tschirch and Ludy¹¹⁶ state that the higher the refractive indices of natural resins the more insoluble or greater the density. Novak and Čech¹¹⁷ have observed the refraction of phenol and formaldehyde reacting to form aqueous and resinous layers. The viscosity of a solution of the reaction mixture in ethyl alcohol was also determined, as well as the bromine value of the reaction mixture. They found that the refractive index and viscosity of the resinous layer steadily increased, whereas the refractive index of the aqueous layer and also the bromine value decreased. Houwink¹¹⁸ considers that in phenol-formaldehyde resins the formation of condensation polymers will be followed by increase in the refraction of the resinous layer. In collaboration with de Boer and Custers¹¹⁸ he found that with an alkaline catalyst there was an increase in the value of K from 0.276 to 0.291. Styrene, however, shows a decrease in the value of K on resinification, which is to be expected from the disappearance of the double bonds. Tung oil at 306° in 7 minutes gave a fall of n_D from 1.5185 to 1.5080. In the writer's opinion (R. S. M.) the drop in value of the refractive index of tung oil is not in agreement with the rise in value when linseed oil is thickened; moreover, it is complicated by the fact that during the gelation of tung oil extensive oxidation occurs, so that

the gelled product is a polymerized oxyn and not a simple polymerized glyceride. Investigation of the absorption spectra of styrene¹¹⁶ showed a displacement to the violet end during resinification, whilst for the cresylic formaldehyde resins it was to the red end of the spectrum. In certain reaction stages a refraction value could be calculated from the absorption measurements, which was in accordance with the empirically determined refraction figures. It is known that the absorption bands of phenol are displaced to the red, when substitution in the benzene nucleus takes place, whereas displacement to violet occurs when the OH group is affected. The observed displacement is in keeping with the proposed formulae for the phenol-formaldehyde resins and for the styrene resins. R. Signer,¹¹⁹ from an examination of the double refraction of the flowing solutions of polystyrenes in chloroform, benzene, &c., and their behaviour in Svedberg's ultracentrifuge, concludes that the polystyrenes are more or less linear.

The study of the optical properties of synthetic resins is of importance, and the further study of the refraction changes during resinification may throw light on the character of the reactions taking place. A. E. Alexander¹²⁰ appeals to manufacturers of synthetic resins to state the value and constancy of the refractive indices of their materials.

DOUBLE-REFRACTION IN TRANSPARENT FILMS

So long as the elasticity limits are not exceeded the double refraction is temporary, since on removal of the tension birefringence disappears slowly, sometimes requiring application of heat. If the effect be permanent a plastic alteration of form has occurred. Thermo-hardening films would show this permanent effect.

It is suggested that the phenomenon of birefringence will become of importance for the investigation of the structures of polymers. Isotropic media often become doubly refractive under certain conditions, e.g. strain, due to orientation of the macromolecules, and the number, colour, and shape of interference fringes provide information as to the stresses and strains produced in the material. If a test piece be locally heated by touching the material, birefringence may be observed with some polymeric materials, whilst others show no effect. Bakelite and similar substances give a powerful double refraction, whereas cellulose esters exhibit only little. In circularly polarized light a light ring and interference fringes may appear and every polymer has its own characteristic image. Stress converts many isotropic materials temporarily into anisotropic crystals or crystallites. In the elastic region there is transitory accidental double refraction caused by the elastic deformation of electron envelopes associated with a change of the Lorentz-Lorenz force between dipoles (cf. p. 491, van der Waals forces).¹²¹ In glass and in rubber the double refraction is proportional to the stress, but for many other polymers these relations are more complicated. For nitrocellulose it is suggested that the material consists of two phases, one elastic and the other plastic. The study of birefringence has proved useful in the elucidation of the initial causes of cracking of paint films;¹²² birefringence is able to show the distribution of internal stresses. Heating may recover the isotropy.¹²³ The importance of birefringence in polymeric materials under the above conditions is of value to elucidate the relations between the effects observed and the molecular structure. Reference must be made to the recent work of investigators, e.g. D. G. Drummond¹²⁴ and J. Spina¹²⁵ on optically esterified anisotropy of cellulose, and W. H. Farwell¹²⁶

on the double refraction and change in length of a vinylite plastic where the birefringence increases almost linearly during stretching and is present to a small extent in the unstretched plastic. A. V. Blom¹²⁷ has discussed the detection of strains in colloidal material, due to internal and external stresses by means of double refraction. The determination of the tension-optical coefficient is recommended as a means of studying the molecular structure of polymerized substances.

If r be the relative retardation between two opposite polarized rays determinable by optical methods, whose refractive indices are n_e and n_o , then for a film of thickness d

$$r = (n_e - n_o)d.$$

$(n_e - n_o)$ is proportional to the tension difference $(\sigma_1 - \sigma_2)$. The tension optical coefficient (Filon) C is given by the equation

$$r = C(\sigma_1 - \sigma_2)d.$$

It may be expressed in Brewsters of dimension 10^{-13} sq. cm. dyn.⁻¹ (Filon). For most plastic substances its value lies between 10 and 100; celluloid = 11, Bakelite 53, but for rubber 2,000, e.g. a cellulose acetate film must be stretched 10 per cent., whereas rubber requires 600 per cent. stretching to give the same optical effect.

The investigation of this material constant is worthy of further study not only with regard to difference in molecular structure, but also in regard to changes set up by temperature, strain, and weathering effects.

REFERENCES

1. H. Staudinger, R. Signer, G. Mie, and J. Hengstenborg, *Z. physikal. Chem.*, 1927, **126**, 425; A., 1927, 647.
2. W. N. Haworth and E. L. Hirst, *Ann. Reports Chem. Soc.*, 1929, **110**
3. P. Karrer and E. V. Krauss, *Helv. Chim. Acta*, 1929, **12**, 1144.
4. K. Meyer and H. Mark, *Der Aufbau der hochpolymeren organischen Naturstoffe* (1930), p. 70
5. *Ber.*, 1929, **62 B**, 2395.
6. *J. Amer. Chem. Soc.*, 1940, **62**, 1561.
7. J. W. Hill, *J. Amer. Chem. Soc.*, 1930, **52**, 4110; W. H. Carothers, *Trans. Faraday Soc.*, 1930, **32**, 39.
8. W. H. Carothers, G. L. Dorough, and F. J. van Natta, *ibid.*, 1932, **54**, 761.
9. J. W. Hill and W. H. Carothers, *ibid.*, 1935, **57**, 925
10. P. J. Flory, *J. Amer. Chem. Soc.*, 1939, **61**, 3334.
11. J. C. Patrick, *Trans. Faraday Soc.*, 1936, **32**, 347.
12. Meyer and Mark, *loc. cit.*, p. 71.
13. General Discussion on the Colloid Aspects of Textile Materials and Related Topics, Faraday Society, Sept. 1932.
14. G. King, *J. Oil and Col. Chem. Assoc.*, 1930, **13**, 28.
15. *Z. angew. Chem.*, 1929, **42**, 76; A., 1929, 542.
16. *J. Amer. Chem. Soc.*, 1928, **50**, 1160.
17. *Helv. Chim. Acta*, 1929, **12**, 934, 958, 964; A., 1929, 1435.
18. *Canad. J. Res.*, 1931, **4**, 344; A., 1931, 833, and *Trans. Faraday Soc.*, 1930, **32**, 315.
19. *Trans. Faraday Soc.*, 1936, **32**, 315.
20. *Trans. Faraday Soc.*, 1936, **32**, 301; *Z. physikal. Chem.* 1933, **165**, 161; *Helv. Chim. Acta* 1934, **17**, 59, 335, 726.
21. *Chem.-Ztg.*, 1930, **54**, 619; B., 1930, 917.
22. *J.S.C.I.*, 1930, **49**, 251 T.
23. *Ibid.*, 1933, **52**, 420 T.
24. *Brit. Plastics*, 1939, **490**, 564, 568.
25. A. J. Weith, *Polymerization* (Burk, Thompson, Weith, and Williams), p. 207.
26. *Ann. Reports, Soc. Chem. Ind.*, 1934, 451.
27. *Ind. Eng. Chem.*, 1925, **17**, 225.
28. *Ibid.*, 1934, **26**, 663.
29. R. Houwink, *Physik. Eigenschaften u. Feinbau von Natur- u. Kunstharzen*, 1934, p. 119.
30. *Ibid.*, p. 123; *Trans. Faraday Soc.*, 1936, **32**, 139.
31. *Trans. Faraday Soc.*, 1936, **32**, 336; *J.S.C.I.*, 1933, **52**, 420 T; 1938, **57**, 189 T, and *Chem. Ind.*, 1939, 99.
32. *Chem.-Ztg.*, 1929, **53**, 493.
33. *J.S.C.I.*, 1938, **57**, 188.

34. *Brit. Plastics Year Book*, 1936, **8**, 65, 197, **9**, 118, 204.
35. *Mod. Plastics*, 1937, **14**, 38, 71; B., 1937, 809.
36. E. L. Holmes and N. J. Megson, *J.S.C.I.*, 1933, **52**, 415 T.
37. N. J. Megson and H. M. Paisley, *ibid.*, 1939, **58**, 213.
38. *Ber.*, 1896, **29**, 2438.
39. *Trans. Faraday Soc.*, 1936, **32**, 382.
40. *Kolloid Z.*, 1931, **57**, 229, and *Brit. Plastics*, 1932, **3**, 498.
41. R. Houwink, *loc. cit.*, p. 25.
42. *Annalen*, 1908, 361, 122.
43. *Trans. Faraday Soc.*, 1936, **32**, 317, 396, 402.
44. *Ind. Eng. Chem.*, 1938, **30**, 1021, and 1939, **31**, 673.
45. *Ber.*, 1926, **59**, 3019.
46. *Brit. Plastics*, 1938, **5**, 238.
47. *Chemistry of Synthetic Resins* (1935), vol. 1, p. 576.
48. Washburn, *Bur Standards J. Research*, 1929, **2**, 476, and K. Hickman, *Chem. Ind.*, 1929, **48**, 365.
49. W. H. Carothers and J. W. Hill, *J. Amer. Chem. Soc.*, 1932, **54**, 1559.
50. J. W. Hill and W. H. Carothers, *ibid.*, 1569.
51. Carothers, *ibid.*, 1579.
52. *ibid.*, 1933, **55**, 4714.
53. J. W. Hill and W. H. Carothers, *ibid.*, 1933, **55**, 5023.
54. Carothers, Dorrough and van Natta, *ibid.*, 1932, **54**, 761.
55. J. W. Hill and W. H. Carothers, *ibid.*, 1933, **55**, 5031.
56. *ibid.*, 5039.
57. *ibid.*, 5043.
58. F. J. van Natta, J. W. Hill, and W. H. Carothers, *ibid.*, 1934, **56**, 455, and J. W. Hill and W. H. Carothers, *ibid.*, 1935, **57**, 925.
59. *Trans. Faraday Soc.*, 1935, **31**, 48; 1936, **32**, 39.
60. W. H. Carothers and G. J. Berchet, *J. Amer. Chem. Soc.*, 1930, **52**, 5289, and W. H. Carothers and J. W. Hill, *ibid.*, 1932, **54**, 1566.
61. Du Pont de Nemours & Co., B. P., 461,236; B., 1937, 471, B. P. 461,367.
62. *Ind. Eng. Chem.*, 1940, **32**, 1560.
63. R. H. Kienle, P. A. van der Meulen, and F. E. Petke, *J. Amer. Chem. Soc.*, 1939, **61**, 2268.
64. *J. Oil Col. Chem. Assoc.*, 1932, **15**, 106.
65. *ibid.*, 1933, **16**, 231.
66. *Varnish Making*, 1939, p. 91.
67. *Ind. Eng. Chem.*, 1938, **30**, 1270.
68. B. P. 500,547; B., 1939, 405.
69. R. S. Morrell and E. O. Phillips, *J. Oil Col. Chem. Assoc.*, 1940, **23**, 103.
70. G. Walter and collaborators, *Trans. Faraday Soc.*, 1936, **32**, 400, and *Kolloid-Beihfte*, 1934, **40**, 158.
71. *Chem. and Ind.*, 1937, **56**, 995; *J. Oil Col. Chem. Assoc.*, 1933, **16**, 231; 1934, **17**, 110, and 1936, **19**, 42.
72. Morrell and Phillips, *J. Oil Col. Chem. Assoc.*, 1940, **23**, 105.
73. *Ind. Eng. Chem.*, 1931, **23**, 1260.
74. *Chem.-Ztg.*, 1934, **48**, 569.
75. *J.S.C.I.*, 1934, **53**, 218 T, and G. F. Goodve, *Trans. Faraday Soc.*, 1939, **35**, 342.
76. *J. Oil Col. Chem. Assoc.*, 1935, **18**, 65.
77. J. R. Katz, *Kolloid-Z.*, 1925, **36**, 300, 1926, **37**, 19.
78. H. Fikentscher and H. Mark, *Kautschuk*, 1930, **6**, 2; B., 1930, 249.
79. H. Staudinger and collaborators, *Ber.*, 1929, **62**, 241.
80. M. Hünenmörder, *Kautschuk*, 1927, **3**, 106.
81. *Physikal. Eigenschaften u. Feinbau von Natur- u. Kunstharzen*, Leipzig, 1934, p. 214.
82. *Der Glaszustand*, Leipzig, 1933.
83. R. Houwink, *Brit. Plastics Year Book*, 1935, p. 51.
84. L. C. Vernon, London Shellac Research Bureau, Technical Paper. No. 3, p. 25.
85. *Trans. Faraday Soc.*, 1936, **31**, 122; *J.S.C.I.*, 1936, **55**, 247 T.
86. J. H. de Boer, *Trans. Faraday Soc.*, 1936, **32**, 10.
87. Id. and H. Hellmann and W. Jost, *Z. Elektrochem.*, 1934, **40**, 806.
88. F. K. Rideal, *Trans. Faraday Soc.*, 1936, **32**, 3, and *Nature*, 1935, **136**, 268.
89. *Nature*, 1940, **145**, 248.
90. *Trans. Faraday Soc.*, 1936, **32**, 97.
91. W. Kuhn, *Kolloid Z.*, 1936, **76**, 258.
92. *Nature*, 1940, **145**, 571.
93. *Chem. Ind.*, 1940, 325.
94. W. Krumphaar, *J. Oil Col. Chem. Assoc.*, 1934, **17**, 413.
95. *Ind. Eng. Chem.*, 1932, **24**, 1068.
96. *Physikal. Eigenschaften u. Feinbau von Natur- u. Kunstharzen*, 1934, pp. 170-88.
97. *Chem. Ind.*, 1938, 3, and C. S. Fuller, *Ind. Eng. Chem.*, 1938, **30**, 472.
98. *Indian J. Physics*, 1930, **5**, 345.
99. *ibid.*, 1928, **3**, 371.
100. Katz and Selman, *Z. Physik*, 1928, **46**, 392.
101. Houwink, *loc. cit.*, p. 188.
102. *Les Applications des Rayons-X*, Paris, p. 230.
103. Bols de Chesne, *Kolloid-Beihfte*, 1932, **36**, 387.
104. *Nature*, 1937, **140**, 642.
105. *Trans. Faraday Soc.*, 1936, **32**, 77.
106. *J. Amer. Chem. Soc.*, 1940, **62**, 1905.
107. C. J. B. Clews, Rubber Techn. Conf., 1938; B., 1938, 948.
108. *Naturwiss.*, 1938, **26**, 387; B., 1938, 1080.
109. S. D. Gehmann, J. E. Field, and R. P. Dinsmore, Rubber Techn. Conf. 1938; B., 1938, 951.

110. H. Barron, *Chem. Ind.*, 1938, 652.
111. A. V. Blom, *J. Oil Col. Chem. Assoc.*, 1937, 20, 199; P. A. Thiessen and R. Spychalski, *Z. physikal. Chem.*, 1931, 156, 435; A., 1931, 1367.
112. *Korrosion und Metallschutz*, 1939, 15, 181.
113. E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy*, vol. 1, p. 362 (1938).
114. T. F. Bradley, *Ind. Eng. Chem. (Anal. Ed.)*, 1931, 3, 304; H. Moore, *Chem. Ind.*, 1939, 58, 1027.
115. R. Houwink, *Brit. Plastics*, 1934, 6, 100.
116. A. Tschirch and E. Stock, *Die Harze* (1933)
117. J. Novak and V. Cech, *Ind. Eng. Chem.*, 1926, 20, 796; 1932, 24, 1275.
118. *Rec. trav. chim.*, 1933, 32, 709
119. R. Signer, *Helv. Chim. Acta*, 1936, 19, 897; A., 1936, 1447.
120. *Ind. Eng. Chem. (News Ed.)*, 1935, 13, 330.
121. I. Fletcher, *The Optical Indicatrix and the Transmission of Light in Crystals*, London, 1892; E. G. Coker and L. N. G. Filon, *Photo-elasticity*, Cambridge, 1931.
122. A. V. Blom, *J. Oil Col. Chem. Assoc.*, 1937, 20, 195.
123. R. Houwink, *Physikalische Eigenschaften u. Feinbau*, u.s.w., Leipzig, 1935.
124. *Nature*, 1940, 145, 67.
125. *J. Phys. Chem.*, 1939, 43, 865.
126. *J. Appl. Physics*, 1939, 10, 109; B, 1940, 62.
127. *Kolloid-Z.*, 1937, 80, 212; A., 1937, 1, 515.

CHAPTER XVII

METHODS OF IDENTIFICATION AND TESTING OF SYNTHETIC RESINS AND OTHER RAW MATERIALS OF PLASTICS

By E. G. COUZENS

Part I. IDENTIFICATION

THE material which is to be identified may present itself in three forms: (1) as a pure constituent or raw material of the plastics or varnish industry, e.g. polystyrene in powder form, or cellulose acetate flake; (2) as a plastic article or processed specimen consisting of (a) the pure constituent, e.g. methyl methacrylate sheet or a polystyrene injection moulding, (b) the plastic constituent modified by the addition of plasticizer, e.g. as a celluloid article, or (c) a thermo-setting resin in its final infusible state, e.g. a bakelite article; (3) in solution as a paint, varnish, or lacquer, along with plasticizers, natural gums, and oils, usually in a mixed solvent.

In the first case a direct examination of the material can be made, but in the other two cases the plastic 'base' may have to be separated from the plasticizer or freed from solvents and gums by evaporation or extraction before a positive identification can be made. The identification of the plastic base in paints, varnishes, and lacquers is more difficult than that of massive plastics; not only because their composition is frequently rather complicated, but also because a wider range of resins is employed. Bradley¹ gives a list of eight types with details of their constituents, properties and applications. They are: polybasic acid polyesters, phenol-formaldehyde condensation products, coumarone-indene polymers, vinyl polymers, chlorodiphenyls, sulphonamide-aldehyde resins, urea-formaldehyde resins, and cyclohexanone-formaldehyde resins.

To these must be added the cellulose esters, most commonly nitro-cellulose, but including cellulose acetate to an increasing extent, cellulose ether in the form of ethyl cellulose, now being used particularly because of its power of dispersing pigments and its wide solubility range, and chlorinated and modified isomerized rubber (Plioform).² The type may include, particularly in the case of polybasic acid polyesters, a very wide range of constituents. Massive plastics are confined to the following simple types: the cellulose compounds, the thermo-setting phenol and urea resins and the vinyls, to which must be added the methacrylates, casein and thiokol.

(1) PLASTICS AND PLASTIC RAW MATERIALS

Preliminary examination. The hardness, stiffness, and colour of the specimen are useful guides to its identity as indicated in the descriptions of the individual plastics, except, of course, in the case of

powdered raw materials when it would be necessary first to mould a sheet or strip.

Much information may be given by simple heating. The following table shows the distinctive character of the results with different plastics:

<i>Material</i>	<i>Treatment</i>	<i>Result</i>
Formvar (polyvinyl formal)	Heated in test-tube	Melts, some discoloration, slight charring, fishy odour, and smell of formaldehyde.
Alvar (polyvinyl acetal)	" "	Melts, some discoloration, slight charring, no smell of acetaldehyde, but this can be detected with Schiff's reagent. Slight fishy odour.
Polyvinyl chloride	" "	Browns immediately, becoming black. Little melting, copious evolution of HCl, detected by smell and ammonia.
Mixed vinylchloride-acetate polymer	" "	As above.
Polystyrene	" "	Melts to clear liquid which boils. Very slight discoloration, characteristic smell of monomer.
Methyl methacrylate	" "	Does not melt or char appreciably, decomposes and monomer distils off.
Bakelite	" " and heated in flame	Presence of wood flour causes much charring and evolution of smoke. This disguises any characteristic odour. Without wood flour phenol and formaldehyde can be detected.
Urea formaldehyde	Heated in flame	Strong smell of formaldehyde and ammonia. Much charring, but highly non-inflammable.
"	Heated in test-tube	Little smell of formaldehyde. Principal odour that of ammonia and pyridine.
Thiourea-formaldehyde	" "	Pronounced smell of H ₂ S and ammonia.
Casein	Heated in flame	Chars readily, pronounced smell of burning protein. More inflammable than urea-formaldehyde. Smell very pronounced and disgusting.
Cellulose acetate	" "	Melts and chars, very pungent smell of burning cellulose and acetic acid.
Ethyl cellulose	" "	Chars, readily melts, smell of burning cellulose together with unpleasant oily smell.
Cellulose aceto-butyrate	" "	Chars and melts. Distinct and characteristic smell of butyric acid.

These results may be obscured in the case of many plastics by the

presence of plasticizers, usually phthalates and phosphates; on warming, the former will give off their characteristic fruity odour.

If castor oil be present, fusion with caustic soda will give capryl alcohol.

Fluorescence. Some further information may be gained from the fluorescence of resins in ultra-violet light.

According to H. Wagner and H. Schirmer,³ pale, powdered synthetic resins show a characteristic behaviour in filtered ultra-violet light: this behaviour varies owing to difference in reflection caused by the size and shape of the particles, and by solvents and plasticizers. Fluorescence tests must be carried out with great care, and the following table shows the behaviour of the pure substance under the quartz lamp, when melted in a test-tube, or, if of a non-melting character, when heated to decomposition.

Fluorescence of Synthetic Resins (molten or heated to decomposition in glass)

H. Wagner and H. Schirmer⁴

Colophony-maleic acid resin	melts, slight yellowish fluorescence.
Modified Albertol resin (phenol-formaldehyde)	" " "
AW2 resin (cyclohexanone resin)	melts, greenish fluorescence.
Coumarone resin, TC-resin	melts, slight violet fluorescence.
Alkyd resin	melts, pale-green fluorescence.
Polystyrol	melts, glass-clear, intense violet fluorescence.
Wacker shellac (phenol formaldehyde and shellac)	melts, no fluorescence.
Acetylcellulose	melts with decomposition, no fluorescence.
Cellulose ethers	decompose, slight "yellowish" fluorescence
Vinyl esters	mainly on undecomposed parts.
Chlorinated rubber	decomposes, no fluorescence.

With the exception of polystyrene all the fluorescent resins are characterized by Storch-Morawski reactions, but the reaction for alkyd resins is not very characteristic.

Solubilities and compatibility relationships. The solubility and compatibility relationship of the resins may be helpful and a very complete review is given by H. Wagner and Schirmer,⁴ but it should be noted that generalizations about solubilities are apt to become inaccurate with alterations in molecular size of the products under test. Thus high-viscosity ethyl cellulose is very difficult to disperse in acetone, though ethyl cellulose is always regarded as soluble in this medium, while the polyvinyl chloride now used in industry has such a large molecular weight that it is practically insoluble in most media, though up to molecular weights of 15,000 it is soluble in toluene.

Qualitative chemical tests. The natural resins are essentially carbon, hydrogen, and oxygen resins, whereas in the synthetic resins nitrogen, sulphur, and chlorine may occur. A sodium fusion should be

carried out and the usual tests for nitrogen, sulphur, and halogens applied. Most of the resins containing nitrogen are condensation products of amines and amides with formaldehyde, nitriles or vinyl-carbazoles; resins containing nitrogen and sulphur may be of the class of 'Beetle' products or Santolite resins. Chlorine may indicate vinyl chloride or chloroacetate polymers, chlorodiphenyl resins or chlorinated rubber. Heating with soda-lime in a stream of nitrogen and passing the vapours into water may often give valuable information by collection of the insoluble volatile material and absorption of the soluble volatile material by water.

G. Bandel⁵ has developed a comprehensive scheme for the analysis of synthetic resins. It is based on a combination of dry distillation, filtered ultra-violet tests, element tests, and saponification numbers, and the matter is dealt with at great length. The special case of vinyl chloride and mixed polymers has been described by H. Doehring.⁶

Chemical colour tests. The original Storch colour test, depending upon the colour developed by sulphuric acid in contact with organic materials and modified by Morawski by the employment of acetic anhydride, has been used by Kraus⁷ to obtain further indications.

A small quantity (a couple of milligrammes) of the resin under test is dissolved in a test-tube with acetic anhydride, with gentle heating. The tube is cooled and a few drops of pure concentrated sulphuric acid allowed to flow slowly down the sides of the tube. The colour which first forms is observed. Nearly all the well-known resins give a more or less intense coloration, with the exception of vinyl acetate and polybasic acid polyesters. After a little while the colour first formed alters, and after about 20 minutes usually disappears altogether. Since, in many cases, the colorations are so intense as not to be transparent, it is recommended that the solution be diluted by the use of an anhydrous indifferent solvent such as benzol or benzine. With a little experience the test can be used for the identification of mixtures of resins with oils, softeners, &c., and so should be a useful aid in the analysis of varnishes and lacquers. Kraus gives results for a number of natural resins under their familiar names, but those he gives for synthetic resins are referred to obscure German proprietary names. A more useful list is given by Wagner and Schirmer.³

<i>Coloration</i>	<i>Resin</i>
(a) <i>Permanent.</i>	
Orange to brownish-red	Coumarone resins (yellow solution in acetic anhydride).
Faint orange-red to rose	TC-resin (no coloration with acetic anhydride).
Deep-brown	Aldehyde resins (yellow soln. in acetic anhydride).
Wine-red	Cyclohexanone resins.
Faint greenish-brown (not decisive).	Alkyd resins.

(b) Changing.

Wine-red, passing to olive-brown

Modified phenol resins; modified maleic acid resins.

Violet, passing to olive-brown

Colophony, resin ester.

No coloration.

Urea resins, phenol resins, vinyl resins, acryl resins, polystyrenes.

The Halphen-Hicks⁸ test only shows definite colour changes with coumarone (purplish-red) and cyclohexanone (intense red). The natural resins show a greater variety of colours, but shellac gives no coloration.

(2) EXTRACTION OF THE RESINS FROM PAINTS AND VARNISHES

Where the resin is dissolved in a varnish the evaporation of the volatile solvent will give a residue which may be tested by the methods already described. If the resins be present as a medium with a pigment the separation from the pigment may be carried out according to the method given by Fox and Bowles.⁸

Bradley¹ recommends a method in which 1 quart of the enamel is diluted with acetone, which dissolves most resins. The mixture may then be filtered through a Buchner filter and the acetone solution evaporated. Clarification can be brought about by kieselguhr. If the material be a lacquer containing cellulose esters, it is desirable to remove these at once and precipitate the cellulose ester by addition of benzene or toluene. The cellulose ester may be redissolved in acetone and again precipitated with benzene or toluene.

Several such treatments may be necessary. Extracted material may be evaporated to dryness at 100–110° or, if high-boiling solvents be present, may be concentrated by a steam distillation. The dried, oily, or resinous extracts are next thoroughly digested with petroleum ether (b.p. 55–75°). Several such treatments may be necessary to remove diethyl, butyl or amyl phthalates, tricresyl phosphates, rosin, &c. The petroleum-ether insolubles are reserved for further examination.

Other methods for extracting resins from lacquer have been described by Gardner.⁹ If the material be a varnish or gum solution (spirit varnish) it may be treated by a steam distillation at 110–120° to remove the volatile solvents. The residue may be dried at the above temperature in an atmosphere of carbon dioxide. It may then be extracted with petroleum ether to remove soluble matter or to assist in the elimination of the last traces of high-boiling-point solvents, which may not have been completely removed by the steam distillation.

All drying operations should be conducted at the lowest possible temperature in order to avoid polymerization or condensation of the substance, and the use of an inert atmosphere is also advisable to

prevent oxidation. The addition of 0.5 per cent. of α -naphthol or of hydroquinone as antioxidants may at times prove of value.

This method for the extraction of resins or vehicles for examination has been found satisfactory in many cases by Bradley,¹ but in some instances the procedure must be varied to meet such conditions as may arise, e.g. by reason of the solubility characteristics, certain resins, such as a phthalic-glyceride or shellac, would be precipitated from a nitrocellulose lacquer together with the nitrocellulose by the benzene or toluene dilution as recommended. This could be ascertained by examination of the precipitated material. Such cases are exceptional and merely show that the analyst must use considerable care in carrying out these operations. The petroleum-ether-insoluble portion of the film-forming solids will generally contain the synthetic resinous constituents, although the examination of the soluble portion is necessary and it may be examined by the same methods as given for the insoluble portion.

Examination of petroleum-ether-insoluble materials. It is advisable to note the relative degree of hardness, softening-point, colour, and relative miscibility at 60 per cent. concentration in the following solvents: 95 per cent. methanol, benzene, ethyl acetate, butyl acetate, cellosolve, turpentine, and naphtha. The solubility and viscosity data of van Heuckeroth¹⁰ should be consulted. The densities and refractive indices may be observed and compared with the values given in the table on p. 505. Bradley lays considerable stress on the importance of the density and refractive index determinations.

The examination of the petroleum-ether-insoluble material may be conducted by qualitative tests for the classes of resins described on pp. 518 et seq.

Quantitative estimation. In view of the great variety of the resins and the difficulty in the estimation of their components or products of treatment with reagents it is extremely difficult to draw up a comprehensive scheme for quantitative examination. A few quantitative values may be obtained, e.g. acid and saponification numbers. For the determination of these values half-normal or normal solutions of sodium hydroxide in methanol may be employed for the saponification, and whenever difficulty is experienced in obtaining solutions, a mixture of equal parts of benzene and a normal solution of alcoholic caustic may be used. As sodium phthalate is sparingly soluble in methanol, Bradley has noted that during the saponification of some phthalate resins crystals of sodium phthalate appear as the saponification nears completion. These may be removed for further examination. If the saponification number be greater than 200, it is probable that the substance comprises or at least contains resinous esters of the polybasic type. Coco-nut oil, highly oxidized oil, and some other esters may yield fairly high saponification numbers, but are generally absent from the usual compositions and will have been detected by other tests.

Polybasic resinous esters may be present even when the saponi-

fication value is less than 200, as when modified by phenolic resins or other non-saponifiable matter. If the material has been indicated to contain or comprise a resin of the polybasic type, it is well to saponify sufficient material to make possible the identification of the several components.

One method for effecting separation of the saponified mixture, according to Bradley,¹ is dilution with water, removal of alcohol by distillation, and acidifying with a mineral acid; after boiling, the free fatty and resin acids are deposited from the aqueous solution. After neutralization by caustic soda the dibasic acids may be precipitated as calcium salts by calcium chloride; phthalic partially, citric, malic, and tartaric acids. Ferric chloride will precipitate phthalic acid more completely, and also benzoic acid and a number of other acids. Lead and silver salts may be formed, and from all the above metallic salts the acids may be identified.

The polyhydric alcohols may be recovered from the filtrate after precipitation of the acids by concentration to dryness and extraction by ether alcohol (1 : 1).

The content of the unsaponifiable matter should be determined and finally the ash content should be obtained.

The above scheme is not a complete quantitative method, except so far as the saponifiable and unsaponifiable material is concerned. The separation of acids from alcohols, &c., gives fractions which have to be examined by qualitative methods.

If the above scheme has shown the presence by qualitative tests of several components, reference must be made to text-books for their quantitative estimation.^{11,12}

It has not yet been possible to carry the quantitative scheme further owing to the great variety of components, whose estimation may be almost of the nature of a research and requires reference to special literature.¹³⁻¹⁵

A method for the quantitative analysis of thermo-hardening synthetic resin moulding compositions developed at the Staatliches Materialprüfungsamt, Berlin-Dahlem, is described by W. Esch.¹⁶ A method for the quantitative determination of resin and filler in a moulding composition is described by Esch and Nitsche.¹⁷

The chlorine in polyvinyl chloride compound can be determined by the method of Piria and Schiff's.¹⁸ This determination is of value in estimating the proportion of vinyl acetate or other monomers such as ethyl acrylate present in polymerized form in polyvinyl chloride copolymer, which may be a matter of considerable importance, as the physical properties of the copolymer are largely determined by the proportion of unchlorinated polymer.

Plasticizers. Plasticizers are frequently incorporated with resins as well as with cellulose esters to modify their physical properties. A great many data regarding their composition and properties are available,¹⁹ but those most commonly used are esters such as dimethyl, diethyl, dibutyl, and methyl glycol phthalates, glyceryl triacetate (triacetin), glyceryl lactate, triphenyl, tricresyl and tributyl

phosphates, chlorinated propyl and ethyl phosphates, butyl tartrate, and triethyl citrate. In the case of nitrocellulose camphor is almost always employed, but is occasionally replaced by diethyl or dibutyl phthalate. Cellulose acetate is usually associated with one or other of the phosphates, one or more of the lower-boiling phthalates and occasionally triacetin. Polyvinyl formal and acetal, polyvinyl chloride, polyvinyl chloride-acetate copolymer, and ethyl cellulose are generally plasticized with phthalate ester and one or other of the phosphates. Polystyrene is an exception, being plasticized either with one of the so-called 'polymeths'²⁰ which are short-chain styrene derivatives, or with an acyl-aryl derivative such as amyl-naphthalene.²¹

Many more substances are available as plasticizers for resins and cellulose, but the ones mentioned are more commonly employed.

Extraction of plasticizer from resin. An extraction apparatus described by W. H. Stevens²² for the extraction of rubber, cellulose, and fats is employed. The apparatus consists of a small, wide-necked, conical flask, fitted with an internal, removable, spiral condenser supporting the extraction thimble, thereby enabling the extract to be weighed in its original container.

Dr. Hetherington in a private communication points out that it is frequently necessary to distil the extracted plasticizer under high vacuum and separate it from low molecular weight polymers which are liable to be extracted along with the plasticizer.

The plastics from cellulose esters can be treated in a special way, owing to the possibility of separating them from plasticizer by precipitating from a dilute acetone solution. For the determination of cellulose acetate in plastic about 0.5 gm. of the plastic is dissolved in 130-50 ml. acetone in a 600 ml. beaker by standing overnight; the evaporated acetone is made up and 100 ml. of equal parts of acetone and alcohol added. 100 ml. of 1 per cent. solution of sodium sulphate is then added to coagulate the precipitate which is stirred to break it up, and the contents of the beaker heated until all the acetone has evaporated. After cooling the precipitate is collected in a Gooch crucible, washed with alcohol and cold water, and finally with 500 ml. of hot water. It is then dried and weighed to give the weight of cellulose acetate free from plasticizer.

The same method can be employed for celluloid, but the dilutions are preferably rather greater, and heating must be continued until all the alcohol has evaporated, and the alcohol wash must be omitted.

The analysis of celluloid can also be carried out by extraction of the camphor with chloroform.²³

DETAILED PROPERTIES OF INDIVIDUAL RESINS

The comparatively simple methods outlined for the general investigation of resins may require reinforcing by more detailed accounts of the various synthetic resins and other classes of plastic materials, and it is necessary, therefore, to summarize them.

Acetaldehyde-polymer resins (Wacker shellac). *General characteristics.* Good electrical properties.

Usual occurrence. In spirit lacquers.

Identification in solid resin. On heating with soda-lime, acetaldehyde or its condensation products are evolved and give a red colour with Schiff's reagent. The resins are saponifiable.

Identification in lacquers (H. Wagner and H. Schirmer).³ Unsaponifiable. For the oil lacquers the unsaponifiable is determined according to the Spitz-Honig method. In the case of nitro-lacquers the nitrocellulose is separated in a small separating funnel with benzine, and run off. The benzine solution is distilled and the resin completely freed from solvent in a drying cupboard. On dry distillation the aldehyde resin may be recognized by its penetrating smell, similar to acetic acid. The distillation may be suitably carried out in a test-tube. The Storch-Morawski test gives a brown coloration.

Alkali polysulphide resins (Thiokol). *General characteristics.* Light-yellow powder, density 1.60, insoluble in all organic solvents. Vulcanized Thiokol mixtures have the characteristic properties of vulcanized rubber, while they have two advantages over rubber, viz. they do not swell in organic solvents which swell rubber, and are not attacked by ozone. They are rendered brittle by alkali hydroxides, are not attacked by dilute HCl, concentrated H_2SO_4 or AcOH, but are attacked by concentrated HCl, HNO_3 and CrO_3 .

Usual occurrence. As a rubber substitute in moulding compositions.

Identification. Recognized by smell and appearance of H_2S on dry distillation.

Alkyd resins (Alkydals, Alphthalates, Duxalkyds, Super-Duxalkyds, Beckosols, Beckolins). *General characteristics.* Easily saponifiable (S.V. 200-60); viscous liquids to hard solids, a wide range of solubilities, usually soluble with difficulty in petrol, hydrocarbons, and ethanol, requiring benzenoid hydrocarbons, ketones, esters, or ether alcohols; some modifications are soluble in petroleum hydrocarbons and ethanols; density, 1.10-1.42; refractive index, 1.54-1.59. Upon strong fusion they usually yield a sublimate of phthalic anhydride, which may be detected by colour reaction.

Usual occurrence. In nitrocellulose lacquers, enamels, varnishes, paints, and surfaces, often in conjunction with aromatic hydrocarbons.

Identification in solid resin. All the phthalic resins show pale-blue fluorescence, but the sulphonamide and coumarone resins also fluoresce. Destructive distillation gives a sublimate of phthalic anhydride. Heating with potassium bisulphate will give acrolein and acetaldehyde. On heating with resorcinol and concentrated sulphuric acid fluorescein is obtained. J. Scheiber²⁴ warms on a water-bath 1-2 drops of the lacquer under examination with a few grains of resorcinol, carefully mixed with $\frac{1}{2}$ -1 ml. concentrated sulphuric acid, the whole having been well shaken together. The mixture is then carefully heated over a free flame until darkening occurs, and after cooling it is poured into excess of alkali. If a phthalic anhydride resin be present a green fluorescence is produced, even if there be a cinder-like separation in the liquid. The test may be tried on the

film material of the lacquer. D. Cannegieter²⁵ recommends heating without sulphuric acid, pouring the melt into dilute caustic soda and boiling, whereupon a green fluorescence appears. He considers this superior to Scheiber's method (loc. cit.) and to that of Bradley,¹ who describes a similar method both with resorcinol and phenol. This opinion is confirmed by F. Kramer,²⁶ who points out that oxidizing agents such as sulphuric acid tend to give fluorescence when heated with resorcinol.

Dr. J. O. Cutter (private communication) states that fluorescence is produced by a heat-treated or oxidized tung oil without the presence of phthalic acid, and the only satisfactory test is the isolation of the phthalic anhydride.

Identification in lacquers (H. Wagner and H. Schirmer).³ The phthalic anhydride and resorcinol tests may also be used here.

Detection of phthalic acid crystals by simple heating. About 2 ml. of the lacquer are freed from solvent by heating slowly in a test-tube over a small flame, then heated more strongly, the resulting vapour allowed to condense in a second test-tube, whereupon large white needles of phthalic anhydride easily visible to the eye crystallize out, and can be recrystallized from benzine solution. The glycerine components may be detected by the pungent smell.

*Detection of phthalic acid by resorcin test according to Storfer.*²⁷ Two porcelain crucibles are heated in a drying cabinet, one containing the substance being tested for phthalic acid (about 2-3 drops), and on the other a blank test is carried out. The two crucibles are supplied with pure resorcin and 6-8 drops concentrated sulphuric acid. They are heated for 5 minutes to 125°, but not above. After cooling, the contents of the crucible are dissolved in 25 ml. water and made alkaline. Phthalic acid shows a yellowish-green fluorescence. From the blank test it can be seen whether the reagents are pure and whether the test has been carried out correctly.

Quantitative methods. Scheiber²⁴ recommends saponification with excess of aqueous or alcoholic potash, removal of alcohol by heat and precipitation of fatty acids, resin acids, and phthalic acid by hydrochloric acid. The fatty and resin acids are extracted with ether, and the phthalic acid washed with ether, dried, and weighed.

A variation of this method is that of Kappelmeier²⁸ which depends upon the formation of phthalate containing alcohol by crystallization. The lacquer under investigation is saponified with alcoholic potash under reflux, and the resulting salt filtered off and weighed. Confirmation of the identity of the compound can be carried out with the resorcin test.

A very detailed method for the analysis of glyptal resins and varnishes is described by A. E. G. Brown.²⁹ Phthalic acid separation depends upon the fact that fatty and natural-resin acids are insoluble in a warm acidified water solution containing a small amount of alcohol, while phthalic acid remains in solution. Fatty and resin acids are extracted with CHCl_3 or CCl_4 and the phthalic acid separated from solution by removal of all the alcohol, 'salting' out, and extrac-

tion with ether. To determine the ratio of fatty acid to phthalic acid take 5 gm. resin (or 10 gm. varnish) and saponify by refluxing 1 hour with 50 ml. 2N alcoholic KOH and 50 ml. benzene. Transfer to a 250 ml. separating funnel, add 50 ml. water, and separate the aqueous layer. The benzene layer should be colourless, but if yellow it should be re-saponified and the fresh aqueous layer added to the first. Dilute the combined water solutions to 200 ml. with warm water and acidify with 5N H_2SO_4 or HCl and extract the fatty acid with $CHCl_3$ or CCl_4 . One 50 ml. portion or two 20 ml. portions should be used. Wash the combined extracts with water and evaporate in a tared dish to constant weight. Make the water solution and water washings slightly alkaline with NaOH, boil down to 20 ml., transfer to a litre separating funnel, dilute to 10 ml., acidify, and add NaCl in excess. Let stand for 1 hour to permit crystallization of the phthalic acid, which is then extracted with methylated ether. Evaporate the ether extract in a tared flask, dry to constant weight, and determine the weight of phthalic acid. When additional drying or non-drying oils are present the separation of the phthalic acid from the fatty acids and natural-resin acids together is identical, and the latter acids are separated as follows: evaporate the solution of these acids to dryness, add 20 ml. alcohol and a mixture of 16 ml. alcohol and 4 ml. H_2SO_4 (concd.), heat under a reflux 5 minutes, transfer to a 250 ml. separating funnel and add 100 ml. methylated ether and 100 ml. 7 per cent. NaCl solution, shake, and allow the two layers to separate. Reject the aqueous layers and shake the ether layer at least twice with 100 ml. 0.2N KOH and 10 ml. alcohol, allowing the layers to separate each time. Remove the aqueous layer to another separating funnel, wash the ether layer with 20 ml. water and 5 ml. 0.2N KOH, and add the washings to the first alkaline extract. Acidify the alkaline solutions with 5N H_2SO_4 or HCl and extract the precipitated natural-resin acids with methylated ether. Reject the aqueous layer and transfer the ether solution to a tared flask. Distil off the ether, add 50 ml. 2N alcoholic KOH, and reflux 1 hour. Precipitate the fatty acids in a separating funnel by acidification, extract with ether, distil the ether, and dry the flask to constant weight to obtain the weight of fatty acids.

Aniline-formaldehyde resins (Cibanit, Panilax). *General characteristics.* Very stable thermoplastic resin of low power factor, impervious to motor spirit, lyes, practically all organic solvents, but not to concentrated organic and mineral acids. Withstands temperatures up to 120° without deformation and is not damaged by temperatures up to 200° , although more or less heavily deformed according to the magnitude of the stress. Density 1.2-1.25.

Usual occurrence. In form of powder, compressed mouldings.

Identification. Aniline-formaldehyde condensation products are partially split up by boiling with 20 per cent. H_2SO_4 , the H_2SO_4 solution is diazotized and coupled up with alkaline soda R-Salt. Appearance of a bright red dyestuff indicates presence of aniline resin.

Chlorinated rubber (Alloprene, Dartex, Pergut, Tegofan, Torneisit). *General characteristics.* Usually a yellowish-white powder of density 1.630–1.660 depending on chlorine content. It is practically odourless, and does not melt under the influence of heat, but begins to char at 150° C. and sinters. It is soluble in aromatic hydrocarbons and in many chlorinated hydrocarbons, higher ketones, nitrobenzene, pyridine, and linseed oil. Insoluble in all aliphatic hydrocarbons and alcohols (methyl to amyl), glycol, glycerol, and turpentine. The solubility of chlorinated rubber in linseed oil is of special importance to the paint and varnish industry, as this material confers special properties on the film owing to its resistance to caustic alkalis and acids. May be produced in any grade of viscosity.

Usual occurrence. Anti-corrosive paints and varnishes.

Identification in solid resin. Scheiber²⁴ recommends the copper-wire flame test. The great resistance to alkalis by chlorinated rubber compounds must be remembered, and a chlorine estimation of the unsaponifiable residue and the high chlorine content, 60 per cent., will be a valuable guide.

Identification in lacquers (H. Wagner and H. Schirmer).³ The lacquer body freed from solvent is mixed with 4–5 times the amount of a mixture of equal parts of potash and soda, and fused. It is kept for 5 to 10 minutes in the molten state. The cooled melt is dissolved in a little hot water, then filtered off and acidified with nitric acid. On addition of 1–2 ml. standard silver nitrate solution a voluminous precipitate of silver chloride is produced. Only a dense precipitate which easily balls together into curds is regarded as a positive reaction. Chlorinated diphenyl and vinyl chloride resins may also show this reaction; however, the former in comparison with chlorinated rubber is soluble in alcohol and benzene hydrocarbons, and the latter on heating does not give the smell characteristic of chlorinated rubber.

*Determination of chemical composition.*³⁰ *Combined chlorine.* About 0.5 gm. of chlorinated rubber, well mixed with 10 ml. concentrated sulphuric acid, is heated for 5 minutes in a boiling water-bath. Chlorinated rubber of low stability will be blackened immediately by this treatment. Highly stable products containing 64–8 per cent. chlorine remain white or at most light grey. This simple test gives an immediate indication of the true stability. Furthermore, the validity of the test is not affected by any traces of carbon tetrachloride remaining in the chlorinated rubber, which may easily indicate a higher chlorine content than the true value.

Chlorodiphenyl resins (Aroclors, Clophene).^{31, 32} *General characteristics.* Not easily saponifiable, but partially decomposed by fusion with caustic alkalis. Partly saponifiable if modified by rosin or oils. May vary from thin liquids to hard, brittle resins or semi-crystalline substances. They have probably a wider range of solubility in organic solvents than any other synthetic resins, with the possible exception of cyclohexanone-formaldehyde resins; soluble in most alcohols, ketones, esters, and hydrocarbons. Melt readily to

liquids of relatively low viscosity. Density generally 1.14–1.8; refractive index, 1.612–1.71, unless modified by other resins and oils; can be distilled readily *in vacuo*. They yield qualitative reactions for chlorine by sodium fusion.

Usual occurrence. In lacquers and varnishes.

Identification. Sodium fusion will detect the presence of chlorine, and destructive distillation will give chlorinated diphenyl (b.p. 250°). The resins are unsaponifiable. Chlorinated rubber gives chlorides on sodium fusion, and destructive distillation yields hydrochloric acid and free carbon.

Colophonyl-maleic acid resins (KM-resin, Alresate). *Identification in lacquers* (H. Wagner and H. Schirmer).³ No possibilities of a smooth detection of maleic acid are recorded in the literature. Wagner and Schirmer (*loc. cit.*) tried to detect it by saponification and precipitation with barium hydroxide; however, the process is uncertain, and the Storch-Morawski reaction which gives a wine-red coloration should be used; rosin ester gives a violet coloration. The colour rapidly disappears and passes into olive-brown. The reaction of cyclohexanone resin is similar. When a mixture of maleic acid and resin ester is present the violet colour is converted into wine-red. In the unsaponifiable portion the different resins containing colophony are not distinguished by the Storch-Morawski test, since all give a wine-red colour.

Coumarone-indene resins (Cumar, Nevindene). *General characteristics.* Non-saponifiable, unless modified by saponifiable material, e.g. rosin or fatty acids. Varnish grades are usually hard, brittle solids, although softer grades are in use. Generally insoluble in ethanol, soluble in acetone, in many esters, and hydrocarbons. Density, 1.10–1.15, but they may range as low as 1.05; refractive index, 1.60–1.66, unless modified with rosin or oils. They may be detected by colour reaction or by liberation of coumarone and indene on destructive distillation.

Usual occurrence. In spirit varnishes, varnishes, paints, and enamels, especially when maximum alkali resistance is desired; often combined with tung oil.

Identification in solid resin. Colour reactions: 0.1 gm. of a coumarone resin is dissolved in 7 ml. of chloroform and 1 ml. of glacial acetic acid, and 1 ml. of 10 per cent. bromine in chloroform is added and the mixture shaken and allowed to stand in a closed vessel; a permanent red colour develops. A less permanent red colour is given by some natural resins. Coumarone and indene produced by destructive distillation will give picrates and mono- and di-bromides of characteristics given herewith:

	Melting-point		
	Picrate	Monobromide	Dibromide
Coumarone . . .	103°	39°	86°
Indene	98°	..	45°

Identification in lacquers (H. Wagner and H. Schirmer).³ *Unsaponifiable*. Identification is by the Storch-Morawski reaction.

The unsaponifiable portion of the lacquer is isolated by the Spitz-Honig³³ method, in which half the benzine is replaced by benzol.³⁴ The unsaponifiable matter is dissolved in a little ether, the ether evaporated off in a test-tube, some glass-wool is placed in the upper part of the test-tube and the bottom heated until copious vapours are evolved. The heating is so carried out that the vapour condenses on the glass-wool. This is then placed in a clean test-tube and acetic anhydride poured over, poured off, and treated with 2 drops sulphuric acid (d. 1.53). Storch-Morawski coumarone gives an orange coloration.

When colophony is also present, as in the case of the resin itself, a violet colour is produced, which can mask the orange colour. Often, however, it is still possible to recognize the coumarone reaction after the fading of the violet coloration. The colour then changes into the correct shade. To facilitate judgement the distillate can be prepared from the unsaponifiable materials of colophony and coumarone resin and this tested at the same time. One part colophony is mixed with three parts coumarone resin and the unsaponifiable prepared from the mixture.

A more certain and simpler method for identifying the coumarone resin in presence of colophony is as follows: the solution in which the Storch-Morawski reaction has been carried out, and which shows an orange coloration when colophony is also present, is placed under the quartz lamp. In both cases the presence of coumarone is recognized by a strong milky violet fluorescence; colophony alone does not give this fluorescence. TC-resin also gives an orange coloration with the Storch-Morawski reaction.

Cyclohexanone-formaldehyde resins (AW 2 resin). *General characteristics*. Generally of a pale lemon colour, somewhat hard and brittle, and of a wide range of solubility in organic solvents, including ethanol and hydrocarbons and oils. The density varies from 1.207 to 1.544. They yield a colour reaction with acetic anhydride and sulphuric acid. Upon strong fusion they yield usually the odour of cyclohexanone (peppermint) and/or formaldehyde.

Identification in solid resin. The colour reactions in the Liebermann-Storch (intense red) and the Halphen-Hicks (intense red) tests are characteristic, and distillation of the resins with soda-lime will give cyclohexanone, recognized by its peppermint odour.

Identification in lacquers (H. Wagner and H. Schirmer).³

Unsaponifiable. When nitrocellulose is present this is shaken out with benzine, filtered off, and the benzine solution freed from solvent by distillation; the residue is taken up in a little ether. In the case of oil varnishes the material is saponified with alcoholic potash and a benzene-benzol mixture used instead of benzine. This solution is freed from solvent by distillation and dried in a drying cupboard at 110°. The residue is taken up with a little ether. A few drops of sulphuric-acid-diphenylamine solution are added slowly to the test-

tube until an orange-red coloration is produced, which indicates the presence of cyclohexanone resin (coumarone resin may show a similar coloration). In the case of oil-free lacquers which are not saponified, the coloration is at first rose-red and then deepens, and without any further addition becomes reddish-violet within a few minutes. The Storch-Morawski test gives a wine-red coloration which scarcely changes.

Melamine-formaldehyde resins. *General characteristics.* Various colours, density of compressed moulding 1.50 to 1.60. Very resistant to dry heat and hot water and hot drinks. More resistant than carbamide mouldings to diluted acids and lyes, and not greatly affected by organic solvents. Compressed product may be manufactured in glass-clear form.

Usual occurrence. In massive plastics and water-soluble varnishes, laminated foils and boards, and glues. In nitrocellulose and alkyd-resin varnishes, and textile finishes.

Phenol-formaldehyde condensation products (Bakelite, Albertols, Beckacite). *General characteristics.* Not very saponifiable, unless modified by large amounts of rosin or fatty acids; varying from viscous liquids to hard brittle solids; solubility varies with the composition and degree of condensation. A few varieties are soluble in ethanol; usually poorly soluble in petroleum hydrocarbons, unless modified by large amounts of rosin or fatty acids, but generally soluble in hydrocarbons, ketones, and esters, unless of the moulding-powder type which, when fully polymerized by heating in a compression mould, is insoluble and infusible. Density, generally 1.2-1.28, unless modified by considerable amounts of rosin, oils, and fatty acids and in the infusible form by fillers; refractive index, generally 1.62-1.69, unless modified by much rosin or oils. Often possess marked odour of phenols, cresols, and/or formaldehyde, especially when heated.

Usual occurrence. Occasionally in nitrocellulose lacquers. In varnishes, enamels, primers, and surfaces, usually with tung oil, spirit varnishes, and cements. These are 'permanently fusible' resins.³⁵⁻⁷ In moulded massive plastics, usually in dark colours, with various fillers such as wood-flour or asbestos, in which form it is rather brittle under impact and infusible and insoluble. In laminated plastics as the impregnating and cementing medium. Also in the form known as Catalin, which may vary from glass-clear water-white solids through transparent colours to mottles in all shades.

Identification in solid resin. Destructive distillation frequently decomposes phenolic resins into their constituents. If the products of decomposition be passed through a cooled U-tube the phenol will condense and the formaldehyde and other escaping gases may be absorbed or washed by bubbling through water. Heating with soda-lime, sodium and calcium phenolates are produced, and a solution of the fused product on treatment with carbon dioxide gives phenol, which can be extracted with ether and identified by colour reactions with bleaching-powder, ferric chloride, &c. Sodium

fusion may be used to detect nitrogen due to the use of hexamine in the manufacture of the resin.

Resins containing ordinary phenol on boiling with concentrated nitric acid give *o-p*-nitrophenol. On diluting and distilling in steam, *o*-nitrophenol distils over as a yellow solid, m.p. 45°, whilst the residue deposits, on cooling, crystals of *p*-nitrophenol, m.p. 115°. Picric acid, m.p. 123°, not volatile in steam, may be formed in some cases. Other phenols are also nitrated. Nitrophenols as a class are characterized by giving an intense orange colour with an alkali.

In a series of articles on practical problems in the manufacture of resinoid plastics,³⁸ a volatility test is described to estimate the amount of uncondensed phenol in phenol-formaldehyde resins; and also the proportion of the resinous matter in which the condensation process has not been carried to a very advanced state. The test consists in estimating the percentage loss in weight of the resin when heated to a high temperature in an inert atmosphere. A fixed weight of the resin is first heated at the temperature of boiling cresol for 30 minutes and the percentage loss of weight determined. This gives the amount of moisture and free phenolic matter in the resin, and usually approximates fairly closely to the phenol figure obtained by steam distillation. The resin is subsequently heated to 300° using benzyl benzoate as the heating medium and the loss of weight again determined. The loss in weight of the sample at the higher temperature may be a measure either of the amount of condensation product present, which is volatile at the temperature at which the test is conducted, or a measure of the amount of volatile condensation product, together with a certain amount of decomposition of a higher condensation product or products. The time taken for the resin to become infusible when heated at this high temperature may also give useful indications of its original state of condensation and its suitability for moulding. This has permitted the setting up of a definite standard in resin manufacture so that deviation from that standard may be detected before the resin has been converted into moulding powders.

In the same article details are given of a test on novolak resins used in the manufacture of high-speed grinding-wheels in the manufacture of which the abrasive is mixed, wetted with about 2 per cent. of furfural and 10 per cent. of the resin (novolak), which has been intimately mixed with sufficient hexamine to act as hardening agent.

Identification in lacquers (H. Wagner and H. Schirmer).³ In absence of colophony, for novolaks, resoles, alnovoles, durophene, and alkyd-phenol resins, the Storch-Morawski reaction is negative; for resin-modified Albertols and Beckacites it is positive. The coloration is wine-red and passes rapidly into olive-brown. The phenol groups may be detected by the following colour reactions: with *p*-nitraniline; the solvent is removed from the lacquer in the drying cupboard, the lacquer body fused with caustic potash in a crucible, kept molten for 5 minutes, the melt dissolved in hot water, and the solution made

acid with sulphuric acid. The phenol is driven off by steam distillation and collected in a receiver. This solution is made alkaline, cooled, and coupled up with diazotized *p*-nitraniline. In presence of phenols a reddish coloration or a red precipitate is produced.

According to Kappelmeier³⁹ 6 gm. lacquer are freed from solvent by evaporation in a porcelain dish and mixed with 20 ml. standard alcoholic caustic potash and evaporated as completely as possible. The contents of the dish are then taken up in 10 ml. of the potash solution, and the liquid obtained, after cooling to room temperature and filtering, treated with 1.5 ml. of reagent freshly prepared by dissolving 0.5 gm. Fast Red salt 3 GL (stable diazo compound of 2-nitro-4-chloraniline) in 5 ml. water and 1 ml. 4N hydrochloric acid. The presence of phenol produces a red coloration or a red precipitate.

Rosin. *Identification in artificial resins.* P. Kampf⁴⁰ tests for rosin in artificial resins by shaking vigorously about 1 gm. of the powdered resin with 10 c.c. petroleum ether and treating the solution with the same quantity of 1 per cent. copper acetate solution. The two solutions are separated and the presence of rosin or turpentine is shown by a greenish-blue coloration due to the formation of salts of copper, soluble in abietic or pimaric acids.

Dr. Cutter (private communication) considers that the only reliable test for rosin is in the isolation of abietic acid or one of its simpler esters, and the editor is in general agreement with him.

Methods proposed by the A.S.T.M. for the sampling and testing of rosin have been described.⁴¹

Sulphonamide-aldehyde resins. *General characteristics.* Usually water-white to pale straw in colour, and may vary from viscous liquids to hard, brittle resins or semi-crystalline solids; density about 1.35, and refractive index 1.596. Qualitative tests for sulphur and nitrogen may be obtained by sodium fusion. Usually they have a marked odour of formaldehyde on heating; generally soluble in esters, ketones, and aromatic hydrocarbons, and insoluble in ethanol and petroleum hydrocarbons.

Usual occurrence. In nitrocellulose or cellulose acetate lacquers, not at present known to occur in oil varnishes.

Identification in solid resin. They are saponifiable and give, on sodium fusion, sulphur and nitrogen tests. The pale-blue fluorescence similar to that of glyptal resins is noteworthy.

Urea-formaldehyde resins (Pollopas, Beetle, Plaskon, Scarab). *General characteristics.* The usual commercial products are extremely hard and tough, insoluble in water and all common organic solvents. Some of the intermediate condensates may occur in aqueous solution and may be used as cements or adhesives. The harder grades have been found to possess density of approximately 1.48, and refractive index 1.66.

Usual occurrence. Mainly in the form of moulded plastics, generally of light colour, the basic resin being colourless, and usually with a cellulose or wood-filler. Also in lacquer finishes, sometimes with alkyd

resins, and in hot-setting glues and cements. Also in laminated plastics, particularly those with a light-coloured finish.

Identification in solid resin. Sodium fusion indicates nitrogen and sulphur in the case of thio-urea resins. On destructive distillation a mixture of amines is obtained which has an alkaline reaction to litmus and a peculiar fish-like odour. The resins are saponifiable. The ureas give ammonia or amines, whilst the thio-urea will give ammonia and an alkaline thiocyanate, which may be detected by ferric chloride.

Identification in lacquers. H. Wagner and H. Schirmer.³ A few grammes of the lacquer containing the urea resin are freed from solvent by heating, and then heated with ten times the amount of concentrated potash or soda-lye under reflux. Ammonia is evolved and is passed into water. The ammonia produced can easily be detected by its smell. Red litmus-paper held at the opening of the vessel turns blue. Or the solution may be neutralized with hydrochloric acid, and the water evaporated off on the water-bath. The ammonium chloride produced can easily be sublimed on heating.

According to L. Metz,⁴² on heating urea-formaldehyde resins with 20 per cent. sulphuric acid, formaldehyde splits off, and can be distilled off with steam, and identified in the distillate by oxidation with iodine in alkaline solution.

Vinyl-resin group.

- Polyvinyl esters (Mowilith, Vinnapas, Luvican),
- Polyvinyl acetals (Formvar, Alvar, Gelva, Butvar, Solvar),
- Polyvinyl acetate-polyvinyl chloride (Vinylite),
- Polyvinyl chloride (Vinoflex, Flamenol, Koroseal, Mipolam, Vinylite),
- Polyacrylic esters (Acronal, Plexigum, Diakon, Lucite, Perspex),
- Polystyrol (Distrene, Styroflex, Trolitul).

General characteristics. Partially saponifiable in some cases. Usually characterized by water-white or very pale straw colour. May vary from rubbery elastic solids to hard, tough solids. Generally soluble in acetone, ethyl acetate, benzene, toluene, and insoluble in petroleum hydrocarbons. Some grades appreciably soluble in ethanol. Usually insoluble in isopropyl ether. Emit a characteristic odour on heating and char easily. Density: above 1.15, vinyl types characterized by a very low refractive index, 1.47-1.48. May be detected by colour reactions.

Usual occurrence. Polyvinyl acetate, owing to cold flow, is not used for plastics, but only for cements. Polyvinyl acetal and polyvinyl formal are used for the production of extremely tough hard sheets by moulding. The acetal also occurs in the form of injection moulding powder. Polyvinyl butyl is used at present solely for safety-glass interlayer. Polyvinyl chloride in the pure form has been developed in Germany in the form of extruded tubes of very high softening-point for plumbing purposes. It is generally dark-coloured

owing to its tendency to decompose when heated. In a highly plasticized form it appears as soft flexible tube and sheet, which is very elastic and non-inflammable. Co-polymerized with vinyl acetate (vinylite) or ethyl acrylate (Mipolam), it is used for the manufacture of thin transparent moulded sheets of great dimensional stability.

Of the polyacrylic esters, ethyl acrylate appears only as a soft, very elastic, and rather gummy material, but methyl methacrylate, characterized by extreme clarity and transparency to light is available chiefly in the form of thick water-white sheets. In moulding-powder form (Diakon) it may appear as transparent mouldings or in very delicate colours.

Polystyrene is either moulded into transparent slabs for electrical purposes or is used for injection moulding to produce clear and coloured mouldings characterized by a glassy tinkle when struck.

In lacquers with or without nitrocellulose; seldom associated with oils or varnish products.

Identification in solid resin. Vinyl chloride or chloracetate resins will have their chlorine detected by the sodium fusion test, but the vinyl acetate resins are free from chlorine. Distillation with soda-lime will give acetaldehyde, uncontaminated with acids. The sodium and calcium salts are formed at the same time and may be examined for acetic acid. The vinyl polymers are saponifiable by alkalis, and the alkaline solution after saponification may be tested for chlorides and acetates. Vinyl acetate in acetic anhydride in the depression of a spot plate will give a bluish-green colour, slowly changing to green on the addition of 2 drops of concentrated sulphuric acid.

Identification in lacquers. H. Wagner and H. Schirmer.³ The detection of these substances is difficult. Vinyl resins and acrylic resins decompose on heating with a brown coloration. Polystyrene melts to a glass-clear liquid which gives a practically blue fluorescence in ultra-violet light.

Rapid detection. The lacquer is freed from solvent in a drying cabinet and heated in a test-tube until white vapour appears. The distillation is so conducted that the pungent vapours are condensed in a test-tube. After about $\frac{1}{2}$ to 1 cm. has distilled over the test-tube is brought under the quartz lamp. The presence of acrylic and vinyl resins is shown by green, and polystyrene by an intense blue fluorescence.

The distinguishing of the vinyl and acrylic resins is carried out as follows: when the above distillate is heated with five times the amount of concentrated NaOH solution it dissolves completely if only acrylic resins are present. In comparison, distillates of vinyl resin and polystyrene do not dissolve.

Vinyl esters can also be detected by saponification. For this, 5 gm. of the lacquer freed from solvent are saponified under reflux with 75 ml. standard alcoholic potash with addition of 2 gm. solid KOH; this takes about 1 hour. The polyvinyl alcohol separates out and after filtration is dissolved in a little hot water. On addition of a

few ml. of a cold saturated borax solution the viscosity is greatly increased, and in the case of vinyl acetate polymers the solution becomes gelatinous. Polyvinyl alcohol itself is said to give a blue coloration in acidified aqueous solution when treated with iodine solution.

Note on Cellulose Esters.

The degree of esterification of cellulose esters is frequently of great importance.

For nitrocellulose, after separation of plasticizers, &c., the nitrogen may be determined by the old but very reliable method of Schultze-Tiemann⁴³, which depends upon the evolution of NO by reaction with ferrous chloride.

The acetyl content of cellulose acetate is generally determined by the method of Barnett⁴⁴ which depends upon the saponification of an acetone solution in the cold.*

Part II. PHYSICAL PROPERTIES OF PLASTICS

Data regarding the physical properties of plastics are of increasing importance as plastics extend the field of their application in industry, and there is now an extensive literature dealing with the determination of these properties and with the actual results obtained.

Every test which is required of a constructional material has now to be considered for plastics, together with certain other tests which are needed on account of the special properties of plastics, some of which, such as cold flow, are disadvantageous, while others, such as ability to flow at high temperatures, are the basis of special processes such as injection moulding.

It is required, therefore, to carry out determinations of specific gravity, tensile strength, limit of proportionality, percentage elongation and the moduli of elasticity, and in certain cases, of shear, or to carry out some form of shearing test. It is also necessary to determine impact strength, compressive strength, flexural strength, softening range, and in the case of moulding materials, flow times, cold flow, and mould shrinkage. Tests for heat shrinkage, water absorption, warping, flammability, resistance to exposure and light are also commonly required and in the case of transparent materials, light transmission and haze.

In the case of lacquers, which are likely to be exposed for long periods to the atmosphere, the effect of light and moisture must be specially studied; hardness or scratch-resistance requires to be

* H. Mark and H. Raff¹⁰⁹ give an excellent summary on pp. 37-47 of the experimental methods used in the identification of synthetic resins. Particular attention is given to a classification according to saponification numbers, and a very useful table based on primary element content is included.

measured, and the viscosity of the constituent plastic is important in relation to body and brushing qualities. Viscosity is also extremely important in film-casting and also as a measure of chain length, which may be of great significance in relation to other physical properties, though this relation is often very obscure.⁴⁵

A list of world organizations interested in standardization of test methods is given by Kline.⁴⁶ This list includes such organizations as the British Standards Institution, the British Electrical and Allied Industries Research Association, the Verband Deutscher Elektrotechniker E.V., and the American Society for Testing Materials, and details regarding their tests have been given by W. D. Owen.⁴⁷ A comprehensive list of tests and of the apparatus employed, chiefly of German origin, is given by W. Zebrowski.⁴⁸ This is an excellent summary apart from its preoccupation with V.D.E. specifications. The same publication also contains a useful list of tests for film by A. V. Blom.⁴⁹

In general, the methods of test employed are based upon those already in use for metals and where possible the results are expressed in the same way. It is found, however, that plastics, except where radically modified by condensation and the use of fillers, as in the case of laminated phenol-formaldehyde boards, are characterized by the phenomenon of plasticity, which among other things, adversely affects the impact test, causes cold flow, and has to be measured, if possible, in order to standardize the flow-properties of plastics.

Plasticity.

The wide bearing of plasticity on industrial problems is illustrated by Freundlich,⁵⁰ who has reviewed the problems peculiar to plasticity, including thixotropy, varnishing, cementing, and glueing, the behaviour of plastic masses and gel formation, and of ceramic masses, without special reference, however, to industrial plastics. These are obviously so called because their industrial use depends so largely upon their plasticity, but the actual measurement of their plastic properties presents considerable difficulties.

Scott Blair⁵¹ has admirably summarized the position with regard to plasticity. He points out that while 'it has no definite dimension and no exact definition' it is, 'although undefinable, associated with certain qualities. The word implies a low viscosity, at least at higher stresses (since the material is easy to mould) combined with a yield value such that shapes can be retained under the stress of gravity.' In the case of industrial plastics much greater stresses than those of gravity must, of course, be resisted. The problem of the different kinds of viscosities of plastics, their measurement, and the determination of the yield value, has been particularly dealt with in two books by Houwink⁵²⁻³ and in more general terms by J. M. Burgers,⁵⁴ who devotes a special section to plasticity from a technological point of view, and it is from their notes that the following account is condensed.

The problem is approached through the study of simple shear, though theoretically experiments on the rate of stretching would be equally applicable for the elucidation of the properties of a substance, especially if they can be performed in such a way that the value of the stress is kept constant during the process. The same is true for rate of deformation under compression, a method which has been actually used by Scott Blair and Coppen.⁵⁵

For certain liquids the effects of simple shear are expressed by the equation

$$D = \frac{dv}{dy} = \phi\tau = \frac{1}{\eta}\tau,$$

where dv is the velocity increment of one plane with respect to another over a distance dy , τ is the shearing force per unit area, and ϕ is a constant, the fluidity, η its reciprocal, the viscosity, and D the velocity gradient.

The curve relating D and τ is a straight line passing through the origin, and liquids which obey this law are called 'Newtonian' or 'simple' liquids.

If, however, the material has a yield value, a portion of the shearing force will be used up in overcoming internal elastic strain, and if the applied force is greater than f , the yield value, the behaviour of the material is expressed by the Bingham formula for purely plastic flow:

$$D = \frac{1}{\eta}(\tau - f),$$

f appearing as an intercept on the τ axis of the diagram. For a detailed discussion of the Bingham treatment see Scott Blair.⁵⁶

There may be cases of liquids which have no yield value but do not give a straight-line relationship between τ and D . In such cases the ratio τ/D is called the viscosity ratio and is written η^* or $\bar{\eta}$ and changes with increase of τ . Such flow is known as quasi-viscous flow, and the relationship can be expressed by the de Waele-Ostwald formula

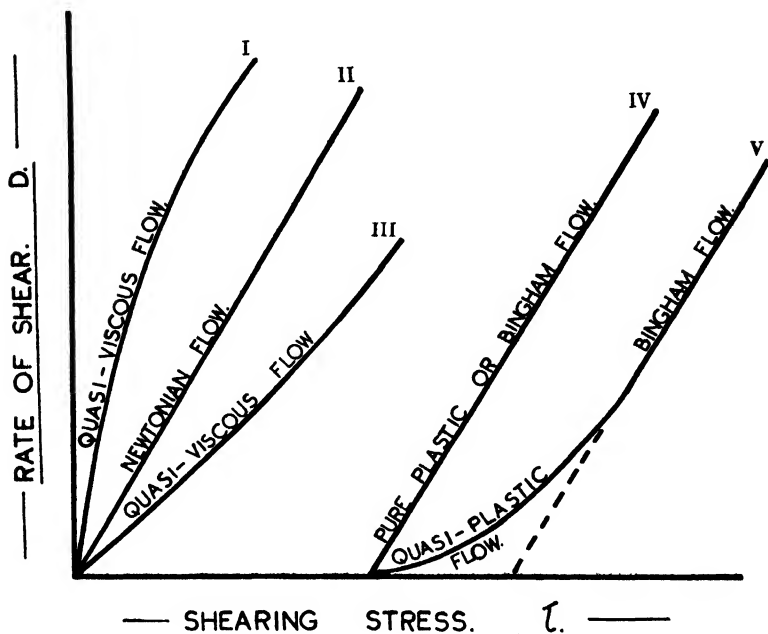
$$D = \frac{1}{\eta^*} \tau^n.$$

By plotting $\log(\text{flow})/\log(\text{pressure})$ curves straight lines can be obtained for many liquids. Ostwald calls this phenomenon 'Struktur-Viskosität', and a detailed account of it has been given by Scott-Blair.⁵⁷

If such a curve has an intercept on the τ axis, i.e. if the material has a yield value, the flow is described as 'quasi'-plastic flow, which can be represented by the Herschel and Bulkley formula

$$D = \frac{1}{\eta^*} (\tau - f)^n.$$

Typical curves are taken from Burgers⁵⁸ and Houwink.^{59*}



In case II the viscosity is constant and independent of τ .

In case III the viscosity decreases with increase of τ .

In case I the viscosity increases with increase of τ .

Cases IV and V have a similar meaning, but here there is a yield value, i.e. a minimum value of the shearing stress below which no deformation occurs at all. All these cases occur in nature, II, for example, in most ordinary liquids, III in clay suspensions and in paints, I in textiles, and V in plastics.

There are two factors which have caused attention to be focused on the shearing-stress/strain diagram. The first is that the Williams parallel-plate plastometer⁶⁰ and its successors afford a very convenient method of measuring applied shearing force and the resulting flow, the second that Scott⁶¹ and Peek⁶² have worked out the mathematical relationship between the observed deformation in the plastometer and the constants in the Herschel and Bulkley equation. The determination of these constants provides a means of characterizing the plastic properties of a material in a manner far superior to the empirical methods of softening range and flow times usually employed, and some important work has been done. Houwink,⁵⁹ for example, has published details of the determination of the constants for phenol

* For a detailed classification of rheological properties see the chart published by the British Rheological Club.¹⁷¹

and cresol formaldehydes and for polystyrene, and has also shown how they alter when P/F resins undergo curing. With Heinze⁶³ he has published details of a simple plastometric method for softening-point, which is later referred to again under that heading, as is also the work of Wearmouth,⁶⁴ who has drawn attention to the possibilities of the plastometer for determining the characteristics of thermoplastics and with Small⁶⁵ has published some interesting results also based on Scott's formula.⁶¹

The subject of plasticity is still a controversial one; for example, the arbitrary division of strain into elastic and viscous components has been criticized by Scott Blair and Coppen,⁶⁶ who have gone back to an equation proposed by Nutting of which, it is pointed out, the Ostwald, de Waele equation is a special case. It is also to be noted that the rates of shear in a plastometer are very low compared with those employed in such processes as injection moulding. The work begun by Wearmouth and Behrenblatt⁶⁷ is also of interest, since they have developed a method of specifying the flow characteristics of thermoplastics by extrusion in a tube at injection temperature.

An important aspect of plasticity is the phenomenon of relaxation. Its practical significance is that it leads to the gradual increase in length of a specimen when it is kept under constant stress; under the influence of thermal agitation the equilibrium is disturbed by relaxation of the interior stress, causing an increase in length until the interior stresses have regained their original value. As Houwink⁶⁸ puts it: 'If relaxation continues this process will be repeated continually, and a state of flow will be reached. It is evident that time plays an important role in deformation processes. A deformation, which when executed quickly is completely elastic, may become plastic if executed slowly.' This is a description of the phenomena reported by Delmonte⁶⁹ in his work on 'creep' and cold flow, and illustrated with regard to its importance in tensile strength determination by Findley,⁷⁰ who has shown that with increased rates of stretching the yield points and fracture stresses of cellulose-acetate plastics greatly increase, while the elongations decrease.

The relation between relaxation time, which is defined as the time required for the applied stress to decrease to $1/e$ of its original value, and elastic modulus and viscosity was first indicated by Clerk Maxwell. Houwink⁶⁸ has briefly discussed this relationship in connexion with the $D-\tau$ diagram, summarizing it in the equation

$$D = \frac{dv}{dy} = \frac{1}{G\lambda}\tau,$$

where G and λ are the elastic modulus and the relaxation time respectively. The product $G\lambda$ takes the place of η in the formula for Newtonian flow.

A more elaborate treatment has been given by de Bruyne⁷¹ which is of particular interest because he has related the $D-\tau$ diagram to molecular size and thermal agitation. He points out that the implication of Maxwell's theory is that the differences between the

elastic behaviour of a solid and a liquid are due to differences in relaxation time and not in elastic modulus, and refers to the work of Hartshorn, Megson and Rushton,⁷² who have found that the viscosity of a number of thermoplastic resins is numerically equal to the product of their relaxation time and a quantity of the same order of magnitude as the modulus of rigidity in the solid state. The variation of relaxation time with temperature must obviously be associated with the development of plasticity. It is given by Andrade's equation⁷³

$$\eta = GAe^{U/RT},$$

where A and U are constants, U being the energy of the bond per gram molecule.

Replacing η by $G\lambda$ we have

$$\lambda = Ae^{U/RT}.$$

De Bruyne has worked out an expression for U in terms of S_0 , the ultimate cohesive stress, V the gram molecular volume, and G , which leads to the equation

$$\lambda = Ae^{(S_0 - S)^2 V / 2GRT}.$$

Maxwell's original analysis permits his equation to be rewritten

$$S = GDAe^{(S_0 - S)^2 V / 2GRT},$$

giving the relationship between τ the shear stress and D the velocity gradient.

If this equation is written in the form

$$X = Y e^{(1-x)^2 / p}$$

X is proportionate to the applied stress, Y to the velocity gradient, and p to T/V . By plotting X against Y for arbitrary values of p straight lines are obtained when p is large, i.e. when the energy of thermal agitation is high and/or the molecules are small. This corresponds to pure viscous flow. With increase of V , i.e. with decreasing values of p , typical quasi-viscous, quasi-plastic or plastic flow curves, with yield values in the last two cases, are obtained.

A description of plastic behaviour covering most of the foregoing and preceded by an account of colloid structure, the methods of research employed, and the results obtained has been given by Horst Müller,⁷⁴ and is probably the best summary at present available.

DETAILS OF TESTS

Specific Gravity.

The only point of importance here is to weigh the sample in a liquid which has no solvent effect on the plastic and is not absorbed by it. The apparent powder density or bulk factor is required for compression moulding powders, and details of the method are given

in the B.S.S. Specifications for phenolic moulding powders.⁷⁵ A method for the determination of density by the usual method is given in the B.S.S. Specification for synthetic-resin varnish-paper boards and tubes.⁷⁶

Tensile Strength, Elastic Limit, Limit of Proportionality, Young's Modulus, and Percentage Elongation.

General. If stress be plotted against strain a characteristic curve is obtained which consists of an initial straight portion over which Hooke's law applies, followed by a curvilinear portion. The point at which this begins is that at which the limit of proportionality between the load applied and the extension measured is reached. It is known as the 'limit of proportionality', and this term is to be preferred to the expression 'elastic limit'.

The yield point is slightly higher than the limit of proportionality, and is the point at which there is an increase of extension without a corresponding increase of load.

Instead of the yield point it is now frequent to determine the proof stress, which is defined⁷⁷ as that stress at which stress-strain curves depart by 0.1 per cent. of the gauge length from the straight line of proportionality. It can be determined by drawing a line from a point on the strain axis corresponding to 0.1 per cent. elongation, parallel to the elastic part of the curve, and reading off the corresponding stress. A description of this test and of the effect of necking in the breaking load is given by Batson and Hyde.⁷⁸

The tensile strength in appropriate units can be calculated from the stress recorded on the machine, divided by the original area of cross-section of the strip. The extension can be obtained either from the strain axis of a diagram where this is plotted by the machine or by measurement of the gap between the jaws.

The stress at the limit of proportionality can also be read off the stress/strain diagram. If this stress be called P , and L and l the original length of the strip and the extension respectively, the latter being also read off the diagram, then

$$\text{Young's modulus} = E = \frac{PL}{l \times \text{area of cross-section}}$$

E is particularly useful as a measure of the rigidity of the material.

A number of machines are in common use for determination of tensile stress/strain relations. Two, the Gardner extensometer and the Schopper machine, are used for films; while for thick moulded or sliced-sheet specimens such machines as the Avery, the Hounsfield tensiometer, the Tinius-Olsen Universal tester, the Denison, and the Ansler machines may be employed.

There are two methods of applying tensile stress to a specimen which differ in that one maintains a constant rate of stretch and the other a constant rate of increase of load.

Both the film machines approximate to a constant rate of stretch type and automatically plot a stress/strain curve, the stress being applied through a motor-driven worm-gear; in the case of the Gardner machine against a spring-loading, and in the Schopper by means of a weighted arm.

Films for testing can be made by casting a solution in appropriate solvents on glass from a hopper in the form of a box of sheet-metal having one short side, leaving a gap of a depth depending upon the thickness of the film required and the concentration of the dope used. After seasoning and checking the thickness by a micrometer, strips can be cut by means of a hand guillotine or stamped out.

The other machines are adapted for testing much thicker samples, which must be machined or moulded to a suitable shape. The Avery machine is a modified form of the usual metal-testing machine; the Hounsfield tensometer employs the movement of a mercury column to indicate the flexure of a spring-bar under the applied load, and this movement can be plotted manually on an extension recording scale actuated by the hand-operated stress mechanism. The Tinius-Olsen machine is motor-operated and plots a curve in the same way as the Schopper. The Denison machine is adapted to give four different speeds of straining by motor-drive, and is also provided with a hand-operated drive. The Amsler machine is hydraulically operated.

All these machines approximate to a constant rate of stretch; the Avery shot machine, on the other hand, is arranged to provide a constant rate of increase of load which is applied by means of fine shot flowing into a receiver at the end of a steel-yard. The Amsler machine can also be arranged by means of an electrical device to give a constant rate of increase of load, while the same effect can be obtained in a special Denison machine by traversing a load at a constant rate along the beam.

The reproducibility of accuracy of the results depends upon the following variables, some of which are discussed by Owen⁷⁹ and in general terms by Richardson.⁸⁰

- (1) The humidity and temperature of the room.
- (2) The mode of holding the test-piece.
- (3) The shape of the test-piece.
- (4) The rate of loading.

(1) Since many plastics are plasticized by water and all thermoplastics are softened by heat, the tests should be carried out on conditioned specimens at standard temperatures.⁸¹ The extreme importance of temperature in the case of thermoplastics has been emphasized by Bartoe,⁸² who has shown that within possible climatic temperature ranges the stress/strain relationship may alter by 100 per cent.

(2) The mode of holding the test-piece is of particular importance in the case of highly plasticized sheet.⁸⁰ The possible effect of serrations in the gripping device should be observed.

(3) The general tendency is to use stamped-out or moulded speci-

men with wide ends, partly on account of the point about the gripping device just mentioned.

For moulded and laminated samples suitable shapes have been developed from cement-testing technique,⁷⁹ and their importance has been emphasized by Mory,⁸³ who showed that the original shape based upon the standard cement sample only gave half the strength recorded by the longer sample now specified.^{75, 84}

A much longer form has been adopted for laminated boards,⁷⁶ for which several specifications exist.⁸⁵⁻⁷ The last-named specification has been discussed by Owen,⁷⁹ particularly with regard to the relation between the overall dimensions and thickness of the sample.

(4) The rate of loading should be specified, for increase in the rate of application of stress in general causes an apparent increase in tensile strength and a decrease in extension. Figures for these changes are given by Bartoe,⁸² and it will be found that time-limits for the duration of the tests are imposed by the specifications cited. The details given by Findley⁷⁰ are of particular interest. For a further study of rate of loading see Couzens and Wearmouth.¹⁷⁰ This question of duration of stress is also of importance in connexion with the length of the specimen, since with constant rate of stretch machines the duration of the test is shorter for short specimens than for long.

Shearing Strength.

Shearing tests are prescribed in specifications for such materials as synthetic resin bonded boards and are carried out by determining the load required to punch a hole of given diameter.⁷⁶ The results are expressed in lb. per sq. in. computed on the sheared area.

Flexural or Transverse-breaking Strength.

The tensile-strength machines, other than those designed for film-testing, can be readily adapted for the carrying out of this test, though special machines, such as the standard Schopper bending-test machine, and the Schopper Dynstat machine,⁸⁸ which is designed for testing small samples, are available.

The general application of the test has been discussed by Chase⁸⁹ and by Owen.⁹⁰ The latter describes the standard Schopper machine and also special apparatus designed by the Bureau of Standards. In all these cases the load is applied centrally, the beam being supported at the ends, and the bending stress S is given by the formula

$$S = \frac{6Wl}{4bd^3},$$

where W is the load, l , b , and d the length, breadth, and thickness of the specimen respectively.

The German specifications⁹¹ require a specimen $120 \times 15 \times 10$ mm. resting on supports 100 mm. apart. The loading is increased at a

uniform rate of 250 kg. per sq. cm. per minute until breakage occurs. There is no corresponding British specification, but laminated materials⁷⁶ are tested in a similar way to withstand a given load without splitting along the laminae. The effect of temperature has been studied by Nitsche and Salewski,⁹² who describe an apparatus for the determination of the flexural strengths of plastics at different temperatures. They examined twenty-six different plastic compositions.

Compressive Strength.

The test as described by Owen⁷⁹ is carried out with any standard compressometer on a specimen moulded, machined, or (in certain cases) built up to the size specified by the testing authority. It is important to have the end faces dead square, flat, and parallel. A small initial load (approximately 100 kg. per sq. cm.) is applied, and the initial length of the specimen read under this load, experience having shown that errors due to dimensional changes caused by bending at the ends are thus reduced to a minimum. The load ultimately measured shall include this initial load. The load is then increased in steps and the yield in each case determined after 1 minute and 10 minutes respectively. The testing machines described can easily be adapted to carry out this test by reversing the motion of the screw moving the cross-head.

The standard set-up may be a percentage compression under a given load⁷⁶ or a load to produce a given compression. In a test of this type⁹³ the Electric Research Association require a minimum load for a 15 mm. specimen that gives a yield up to 5 mm., which is computed from the following formula:

$$\text{yield} = y + \frac{0.25y}{y'}$$

where y and y' are the yields in mm. at 10 minutes and 1 minute respectively.

This test, particularly when carried out on thermoplastic materials, has been shown by Bartoe⁸² to be very sensitive to rate of application of load and to temperature.

Details of specimens are given by Owen^{94, 95} and by Chase.⁸⁹

Impact Strength (Toughness).

Resistance to impact is measured by the energy absorbed in the breaking of a strip by a swinging hammer. The strip may be supported at one or both ends, and may be notched or unnotched.

Support at one end is characteristic of the Izod machine, while the Charpy machine strikes a blow at a strip supported at both ends. Both machines are described by Owen,^{90, 95} and the American practice by Chase,⁹⁶ and the German Schopper machine, in detail, by Scheiber and Sändig.⁹⁷ In all cases the blow is delivered by a swinging hammer, the total energy of which is about 2 ft.-lb. The Schopper machine has

an alternative hammer-head of about one-quarter this energy for weaker materials. Schopper also make a 'Dynstat' machine for small samples.⁸⁸ Avery have recently developed a special machine for plastics made in three sizes, 1 ft.-lb., 3 ft.-lb., and 10 ft.-lb., the large size being required only for the toughest 'filled' materials.

The energy required to break $\frac{1}{2}$ in. square specimens of commonly used plastics varies from 0.10 to 1.0 ft.-lb. when the bar is notched to a depth of 0.10 in., and since it is not possible to correlate breaking energy with cross-section, specifications give exact dimensions for specimens and for the position and dimensions of the notch.^{75, 84, 98} For a discussion of the design of a machine see Hopkins.⁹⁹ The object of the notch, the dimensions of which are of the greatest importance, is to concentrate the stress at one point.⁸⁰ The correlation of the results from notched and unnotched specimens with field experience has been critically discussed by Burns and Werring.¹⁰⁰ These authors find that while notching gives a better relationship to experience and recommend it both for Izod and Charpy tests (of which they prefer the former, because it uses less plastic, and the pieces do not get in the way of the hammer), the actual correlation of the results with field experience is not satisfactory, even when the tests are carried out on a series of specimens of the same type of plastic. When an attempt is made to compare widely different types, the discrepancies become greater still. They conclude, in fact, that by itself the impact test is useless, but that consideration of notched and unnotched tests with flexural strength results, which cannot be correlated with impact tests, is the best guide to behaviour in the field. When all three figures are high, good results are obtained for articles made of the plastic in question.

A very interesting contribution to the theory and practice of the impact test has been made by Southwell and his contributors.^{101, 102} The objections to the standard pendulum are:

- (i) that its rigid construction permits a transmission of energy to earth;
- (ii) that in the Izod test a shearing component is superimposed on the bending moment, while in the Charpy test the stresses can only be conjectured;
- (iii) that the striker being usually in the form of a blunt knife penetrates the specimen to a considerable depth, involving a considerable amount of plastic distortion, very complicated in type, which accounts for a considerable part of the measured energy of fracture.

The authors, overcoming these difficulties, obtained highly consistent results by using:

- (i) a ballistic type of pendulum, known as the Oxford machine;
- (ii) a four-point loading of the specimen;
- (iii) a specimen of circular cross-section with a concentric groove.

So far this machine has not been applied to plastics, but the points raised by the authors should be even more important for plastics than for metals.

Toughness.

Since the impact test is rather unsatisfactory, it has been proposed by Andersen¹⁰³ that toughness should be expressed in terms of a 'tensile product', i.e. a combination of tensile strength and elongation. Bass and Kauppi¹⁰⁴ have also discussed this proposal and illustrated it in terms of ethyl cellulose. There is no doubt that it has much to recommend it, but it has not yet been adopted in any specifications.

Hardness and Scratch Resistance.

The general subject has been discussed by Pitzer,¹⁰⁵ who points out that tests are of four types: (a) penetration, (b) abrasion, or scratch tests, (c) cold flow, (d) machinability.

(a) *Penetration tests.* These tests may be divided into three classes: (i) spherical or ball indentations, (ii) prism or cone indentations, (iii) rebound tests.

(i) *Indentations with spheres.* The best known of these are the Brinell, Rockwell, and Martens tests, but the Martens test has not received much attention for plastics.

The Brinell method has been described by Owen¹⁰⁶ and gives a number called the Brinell hardness number which is obtained by dividing the area of the indentation made by a sphere by the load which causes it. It is not satisfactory with laminated materials, as they tend to ridge. For other plastics the factors are time, size of sphere,^{107, 108} which is generally fixed at a diameter of 2.5 mm., and the load, which may be from 25 to 500 kg. The Rockwell test is based upon the increment of depth of penetration resulting from increasing a minor load pressure to a major load pressure, and though particularly sensitive to the time factor is incorporated in American specifications.^{109, 110} The Rockwell and Brinell numbers can be mutually converted.¹¹¹

(ii) *Indentations with prisms or cones.* As pointed out by Kline and Axilrod,¹¹⁰ a pyramidal or conical tool gives a load/area quotient (or hardness number) which is substantially independent of the load, and for this reason they prefer the Vickers machine, which they compare critically with the Brinell and Rockwell instruments. The tool here is a square pyramid having an angle between opposite faces of 136°; the load is applied gradually, maintained for a given time, say 10 seconds, and automatically removed. The indentation is then measured with a microscope which can be located exactly over the impression.

(iii) *Rebound Tests.* The best-known instrument is the Shore Scleroscope discussed by Williams,¹¹² and some details are given by W. D. Owen.¹⁰⁶

A small diamond-pointed hammer $\frac{3}{4}$ in. long and $\frac{1}{4}$ in. diameter, weighing 1/12 oz., falls through 10 in. on to the specimen and the height of the rebound is measured against an arbitrary scale of 140 divisions. On the 'Scleroscope' scale martensite high carbon steel equals 100 and may be regarded as a standard of reference. So far its use in plastics has not been extensive.

(b) *Abrasion or Scratch Tests for Surface Hardness.* These tests are carried out either by direct scratch methods or by measurement of reduction of oscillation of a pendulum swinging about a pivot resting on the plastic surface.

The best direct method is that of Bierbaum's 'Microcharacter' the operation of which is described by Kline and Axilrod.¹¹⁰

The scratch is made by a diamond in the form of a corner of a cube with its diagonal normal to the surface under test, and the scratch-resistance is reported as the quotient of the load in kilograms divided by the square of the scratch width in millimetres.

The scratch-resistance thus calculated is found to be substantially independent of the load and consistent results are obtained.

Chase¹¹⁴ describes other special methods, such as that of Burns, of the Bell Telephone Laboratories, who used a method correlating scratch depth and tensile strength, and an Eastman Kodak method devised by S. E. Sheppard and J. J. Schmitt,¹¹⁵ who not only describe the method but also give an interesting account of the effect of plasticizers.

This method gives scratch-susceptibility in terms of the load just producing a scratch, or by a curve expressing the relation between the magnitude of the load and the scratch. It is specially adapted for the measurement of thin films of cellulose derivatives on glass. There are a number of pendulum methods. Chase¹¹⁴ describes the Herbert type; two other methods, the Walker-Steele swinging beam method and the Sward rocker¹¹⁶ test, are described by Gardner.¹¹⁷

These pendulum methods depend upon the reaction between the plastic surface and a pivot, such as a spherical surface of small diameter carrying a beam oscillating about this pivot.

In the Walker and Steele method the time required to decrease a given oscillation to half-value is compared with the same effect on a glass surface, while the Sward rocker depends upon the observation that the angular movements are proportional to the hardness of the material. So far these methods have been mainly applied to varnish films rather than to massive plastics.

Plasticity: Softening-point or Plastic Yield.

Since plastics do not have a definite softening-point, arbitrary conditions have to be laid down for deformation tests which serve as a basis of comparison of different plastics. British, American, and German specifications are in force, all based on the deformation of a loaded bar, but the details differ. In the British test⁷⁵ a loaded cantilever specimen, after a pre-heat of 15 minutes, is heated at a given temperature for 6 hours. The plastic yield must not be more than 5 mm. The yield temperature is obtained by interpolation from temperature/deflexion curves.

The German or Martens test⁹¹ is described in detail by Zebrowski.¹¹⁸ A rectangular bar is clamped vertically at one end and a bending force of 50 kg. per sq. cm. applied. The temperature is raised 50° C.

per hour till the deflexion reaches 6 mm. The American test^{119,122} resembles the German. The yield temperature is taken as that at which the deflexion is 5 mm. and is known as the Martens number.

The German method is more rapid than the British but usually gives too high a result, owing to lack of allowance for the time factor. The two tests have been critically compared by Owen.^{120, 121}

A further German test is the Vicat needle test, also fully described by Zebrowski¹¹⁸ and by Owen,¹²² and particularly recommended as a guide to behaviour with screws and rivets. It consists in the measurement of the vertical penetration of a plastic by a loaded steel needle, with rise of temperature at the rate of 50° per hour, the Vicat number being the temperature at which 1 mm. penetration has taken place.

A penetration method has also been proposed by the A.S.T.M.,¹²³ and a deformation method known as the 'ring and ball',¹²⁴ which, however, requires high temperatures with consequent polymerization of phenolic resins.

Flow Time and Temperature.

Two types of test have been put forward, one based on flow through orifices and the other on deformation in parallel plate plastometers.

Flow Tests.

These tests have been empirical in character. Attempts have been made to set up flow tests based on a standard moulding,¹²⁵ by Forrer on extrusion along a spiral groove,¹²⁶ and by Krahl along a nozzle,¹²⁷ but the most elaborate is the Olsen Bakelite flow tester of Rossi and Peakes,¹²⁸ described by Penning and Meyer.^{129,130} In this instrument there is a vertical orifice in a split cone above a charge chamber on a steam-heated block. A ram works in the charge chamber up to 3,000 lb. per sq. in., and means are provided for regulating and observing the temperature of the orifice and of the charge chamber. The amount of material extruded in the orifice is automatically recorded on a revolving drum.

For thermoplastic materials a flow classification is made by determining the temperature at which each standard material has a definite length of flow, and these temperatures are plotted against the corresponding flows at, say, 275° F. Samples to be classified are then run at 275° F. and the actual flow at this temperature used to determine the classification. This method has been used as the basis of a test by the American Society of Testing Materials¹³¹ which has been discussed in detail by Meyer.¹³²

In contrast to those empirical methods, D - τ relations have been studied by Dillon and Johnson¹³³ and are being developed by Wearmouth and Behrenblatt.⁶⁷

Special methods and apparatus for the study of thermo-hardening resins have been described by Krahl¹³⁴ and Schmittmann,¹³⁵ and the subject has been generally reviewed by K. Brandenburger.¹³⁶

Plastometer Tests.

The Williams plastometer, already mentioned,⁶⁰ is the basis of the apparatus used for these tests and its many variations have been fully described by van Nieuwenburg.¹³⁷ An early use was by Karrer,¹³⁸ who attempted to distinguish between plasticity and elasticity by short compression in a plastometer, but its most direct application to the practical problems of the study of the plasticity of hardening resins is by Houwink and Heinze,⁶³ who use the deformation, after 30 minutes' compression by a 5 kg. wt. of a 10 mm. sample, for comparing resins. For thermoplastics it has since been used by Wearmouth and Small⁶⁵ to determine the value of f the yield value for a number of materials, and so to give a far more accurate forecast of the safe limiting temperature at which the material may be used than can be obtained by the Martens or similar tests. The method is also recommended for the study of plasticizers.

An entirely different method, of particular use in connexion with the mixing of plastic doughs, is that of the Brabender plastograph,¹³⁹ which reproduces mixing conditions and measures resistance to shear. Speitman¹⁴⁰ has given details of its application to phenol and urea-formaldehyde and glyptal resins.

Cold Flow.

The cold flow or deformation of plastics at room temperature under load is of great importance. It has been studied by Burns and Hopkins,¹⁴¹ who have measured the average rates of flow at 120° F. for 24 hours of $\frac{1}{2}$ in. cubes under a load of 1,000 lb. and give instances of the correlation of behaviour under this test with field behaviour. The method is really that of a parallel-plate plastometer, and the percentage change in height of the cube or of pile-ups is taken as the value of the material. Delmonte⁶⁹ has carried out cold-flow tests using the A.S.T.M. loaded beam method for softening-point¹¹⁹ and has shown that flow takes place in two stages—creep, which is greatest following elastic deformation, and cold flow, which is a constant rate of change of deformation which a material will exhibit indefinitely after being subjected to a certain stress for a certain period of time at constant temperature. He has developed a general equation expressing plastic deformation rate as a function of a coefficient of viscous resistance and of a coefficient of internal resistance, thus emphasizing the dual nature of the structure of plastics, the elastic deformation occurring as well as a time-dependent plastic deformation even at very low stresses.

The phenomenon of creep in plastic-impregnated fabrics has been discussed by de Bruyne,¹⁴² who shows that the divergence of such material from Hooke's law when stressed is due to creep which can be controlled by imposing a tension on the filler in such a way as to exert compression on the resin, materials of very high elastic strength being thus produced.

Heat Shrinkage.

This test is useful as a guide to the effect of loss of volatile content, such as plasticizer or residual solvent. As specified for clear transparent acetate sheet¹⁴³ it consists in heating the specimen in the form of a 10 in. strip, 1 in. wide, in an oven at 60° for 24 hours. Though not specified, it is obvious that the strip should be conditioned before and after the test. It is open to the criticism that the thicker the sample the lower the proportion of the actual shrinkage to that which is possible. Conditioning is usually assumed to be satisfactory after 24 hours' exposure to a given relative humidity, but this again depends on the thickness of the specimen and the plastic concerned, and should be checked by weighing until constant weight is attained.

Mould Shrinkage.

Mould shrinkage is expressed in thousandths of an inch per inch and can be obtained by comparing the diameter of a moulded disk with that of the cold mould from which it has been made.⁷⁵

Warping.

The tendency to warp in high humidities can be observed and a standard set up¹⁴² by exposing a 2 in. moulded disk, 0.06 in. thick, to the action of water vapour. The disk is laid horizontally on a glass plate over a vessel containing water at a level of about 1 in. below the plate with $\frac{1}{2}$ in. of the disk projecting over the water. It is maintained in this position at 100° F. for a given time, say 5 days, and the resulting warp measured by pressing one edge of the disk flat and scaling off the elevation of the opposite edge.

Water Absorption.

This is a difficult test to specify, since

- (a) duration of the test and the thickness of the specimen must be properly correlated,
- (b) in certain cases, particularly that of the cellulose esters, a leaching process takes place, which causes a loss of weight, which offsets the gain of weight through water absorption.

The British specification for transparent cellulose-acetate sheets¹⁴³ is concerned only with the change in length of the specimen, as a result of 24 hours' immersion in water and of subsequent drying at room temperature, but a tentative method put forward by the A.S.T.M.¹⁴⁵ takes account of the increase in weight resulting from the immersion of a *dried* specimen, and provides, in addition, for a determination of any resulting loss in weight by weighing the specimen after redrying. Two temperatures, 50° and 110°, are specified, depending on whether the plastic is likely to have its water absorption value affected by high temperatures or not. In general $\frac{1}{8}$ in. is specified as the thickness of the specimen, but no provision is made

for determining whether water-absorption is complete or not. Fordyce and Meyer,¹⁴⁶ in a study of plasticizer-compatibility with cellulose acetate and cellulose acetobutyrate, have used a method resembling that of the A.S.T.M. for determining the effect of plasticizers on water absorption and the leaching which takes place. They also give data for solubility of plasticizers, which by correlation with leaching data indicate that compatibility is the controlling factor rather than solubility.

Drying the samples to obtain the leaching loss was carried out at 55° and the magnitude of the losses so observed indicates their great effect in apparent water absorption.

Flammability.

The British specification for transparent cellulose-acetate sheets¹⁴³ describes a test for flammability which requires a 10 in. strip of plastic to be supported vertically by means of a 1 in. square of ciné film cemented to the top end of the specimen, which is ignited by means of another 1 in. square ciné film cemented to the lower end. After ignition of the lower square of ciné film, the flame must extinguish itself before igniting the top square of film, while burning in still air. The German test for 'Glutfestigkeit'¹⁴⁷ described in detail by Schramm and Zebrowski¹⁴⁸ involves the application under a definite pressure of an electrically heated rod at 510° to the end of the specimen. The loss of weight and the length of burning is measured. The older 'Feuersicherheit' test⁹¹ consists in the application of a special Bunsen flame to the specimen and measurement of the time during which combustion is supported. Similar tests are applied in British¹⁴⁹ and American¹⁵⁰ specifications for insulating materials.

Thermal Conductivity, Thermal Expansion, and Specific Heat.

The determination of these physical properties belongs rather to the domain of pure physics. A general discussion of the methods and difficulties involved has been published by Owen¹⁵¹ and later by Zinzow,¹⁵² who gives many further references.

There is, however, an American specification for the determination of conductivity¹⁵³ of solid electrical insulating materials in which the temperature drops of a recording plate, separated from a hot plate by a disk of known conductivity and of the material to be tested respectively, are compared.

Resistance to Light.

Kline¹⁵⁴ has discussed the validity of the carbon arc and the mercury-vapour lamp as an accelerated ageing-test for protective and decorative coatings in lieu of sunshine. He concludes that they are not to be relied upon to give exposure tests comparable to fence or rack exposures in the open. On the whole the carbon arc is the better,

but temperature is important. Gardner¹⁵⁵ has devised a rotating rack in which the sun's rays are perpendicular at all times. In American conditions fading, chalking, and checking which would take 6 to 8 months are produced in 6 to 8 weeks in this apparatus.

For the light-testing of transparent plastics for aircraft see Axilrod and Kline.¹⁵⁶

Clarity.

The simplest method of determining the clarity of a plastic is to project a beam of light on to a photo-electric cell with and without the interposition of the specimen in the beam. The microammeter readings of the current generated in the cell are then proportional to the light transmitted and the percentage transmission can be directly calculated.¹⁵⁷

There are, however, three important considerations of which this method takes no account.

- (1) There may not be a linear relationship between illumination and current generated in the photo-electric cell.
- (2) The sensitivity range of the cell may not be identical with the visual range, nor may it be constant for any one type of cell.
- (3) No account is taken of the effect of scatter.

How great this may be can be observed from a consideration of the case of frosted glass, which, close to an electric cell, transmits about 70 per cent. of the incident light, a percentage which rapidly falls off as the cell is moved farther away.

The first difficulty can be overcome by the 'null' method as used for bullet-proof glass.¹⁵⁸ The light beam is not collimated, for the method depends upon the fact that the intensity of light from a point source is proportional to the square of the distance.

If a = initial distance of a lamp from a photo-cell and

b = movement of the cell nearer the lamp required to give the same reading when the plastic is interposed,

$$\text{per cent. light transmitted} = \frac{(a-b)}{a^2} \times 100.$$

The second point, that of sensitivity, can be dealt with by means of a suitable filter. The range of wave-lengths to which the human eye is sensitive is from 400 to 700 millimicrons with a peak at 555, whereas a cell has a much wider range of sensitivity; Fogle¹⁵⁹ has described Corning glass filters suitable for this purpose and manufacturers now supply filters such as the 'Viscor' filter for use with Weston photronic cells.

The third point, that of scatter, can be met by the use of a two-aperture system.^{160, 161}

A 6-volt auto-bulb in a cylindrical housing, or better still operating with a collimator, directs a parallel beam through a 1 in. aperture A . A second 1 in. aperture B is situated 18 in. away from A and $1\frac{1}{2}$ in.

behind this is the cell, fitted with a suitable filter. The light is adjusted to give a prearranged fixed deflexion on a microammeter and the sample is then placed in front of aperture *B*, i.e. close to the cell.

$$\text{Then the light transmitted} = \frac{\text{deflexion with plastic at } B}{\text{full deflexion}}.$$

The scatter or haziness can then be measured by taking a second reading with the sample in front of *A*

$$\text{haziness} = \frac{\text{deflexion at } B - \text{deflexion at } A}{\text{deflexion at } B}.$$

This method is still open to the first objection, that it depends upon the accuracy and constancy of the cell, and this can only be met by spectro-photometric measurements.

Viscosity.

The literature of viscosity is immense, but for the practical problems connected with varnishes and dopes the methods are comparatively simple and have been satisfactorily dealt with through the publication by the British Standards Institution of a standard method¹⁶² for its determination in c.g.s. units. That a viscosity should be expressed in absolute units cannot be too strongly emphasized, as only thus can comparisons be made and conclusions as to molecular size, &c., be drawn.

The units of measurement are:

for the dynamic viscosity η —the poise (*p*);

for the kinematic viscosity ν —the stokes (*s*).

The centipoise (*cp*) and the centistokes (*cs*) are $\frac{1}{100}$ ths of these units respectively, and the relation between the units is

$$\nu = \frac{\eta}{\rho},$$

where ρ = the density of the fluid.

Two methods are employed, the U-tube viscometer and the falling sphere.

U-tube Viscometers. These viscometers are of an Ostwald type, having bulb reservoirs above a capillary of predetermined length. Five different sized tubes are specified, covering a range of from 0.5 up to 1,500 centistokes, and a method is described for calculating the two constants *C* and *c* in the equation

$$\nu = Ct - c/t$$

where *t* is the time required for a given volume of liquid to flow through the capillary, *C* is a constant for the apparatus and *c* a constant which corrects for kinetic energy of efflux, according to Poiseuille's equation.

C can be calculated from the observed time t of flow of a liquid of known viscosity ν from the equation.

$$C = \frac{\nu}{t} + \frac{c}{t^2}.$$

For more viscous liquids U-tube viscometers are described in which mercury is drawn into a bulb reservoir above a capillary in one limb of the apparatus, the rest of the U-tube being filled with the liquid to be examined.

The time taken for the liquid to be driven upwards through a capillary in the other limb by the fall of the mercury on release of the vacuum is then taken.

If this be t ,
$$\nu = Kt(1 - a\theta - f\rho)/\rho,$$

where K and f are constants of the instrument, a the coefficient of expansion of mercury, ρ the density of the liquid, and θ the temperature.

K is determined by calibration with liquid of known viscosity and density and f is calculated from the mean heads of the liquid and the mercury above the interface.

Falling Sphere Viscometers. For ranges from 1,000 to 25,000 centistokes a sphere of diameter from $\frac{1}{16}$ to $\frac{1}{8}$ in. depending on the viscosity is timed as it falls over a distance of 150 mm. in a tube filled with the liquid and having an internal diameter *not less than ten times* that of the sphere.

If t = time in secs. to fall s cm. (= 15 cm.), then

$$\nu = t \left\{ \frac{d^2g}{0.18s} \left(\frac{\delta}{\rho} - 1 \right) \left(1 - \frac{2 \cdot 1d}{D} \right) \right\},$$

where d = diameter of sphere in cm.,

δ = density of sphere in gm. per cm.³,

ρ = density of liquid in gm. per cm.³,

D = diameter of tube in cm.

For the same sphere and fall-tube this may be simplified to

$$\nu = Kt(\delta/\rho - 1),$$

where K is $\frac{d^2g}{0.18s} \left(1 - \frac{2 \cdot 1d}{D} \right)$ in the above equation, or may be obtained from experiment with a liquid of known viscosity.

A simple method of determining dynamic viscosities (poises) without density determination has been developed by Farrow¹⁶³ from an original method of Scarpa.¹⁶⁴

The method depends on the movement of the liquid under examination up and down a capillary tube. If the times be t_1 and t_2 respectively,

$$\eta = \frac{Kt_1 t_2}{t_1 + t_2},$$

where K is a constant determined by means of a liquid of known viscosity.

A quick method of comparison for materials of the same class is the air-bubble viscometer of Barr.¹⁶⁵ If the diameter of the tube selected gives a suitable slow rate of use, the time for the bubble to travel over a given distance varies as η . The method is most suitable for liquids of high viscosity which permit the use of wide tubes, as the surface tension effect is then at a minimum.

For a detailed study of the falling sphere viscometer Gibson and Jacobs may be consulted.¹⁶⁶ They recommend pure glycerine at 20° with a density of 1.2589 as a standard, having a viscosity of 10.24 in absolute units.

For a survey of viscometry in general, reference should be made to Barr's Monograph¹⁶⁸ and for synthetic resins¹⁶⁹ to H. Mark.

REFERENCES

1. T. F. Brudley, *Ind. Eng. Chem*, Anal. Ed., 1931, 3, 304.
2. H. R. Thies and A. M. Clifford, *Ind. Eng. Chem*, 1934, 26, 123-9.
3. H. Wagner and H. Schirmer, *Farben-Ztg.*, 1938, 43, 131-3, 157-8.
4. *Ibid.* 131-3.
5. G. Bandel, *Angew. Chemie*, 1938, 51, 570-4; B., 1938, 1190.
6. H. Doehring, *Kunststoffe*, 1938, 28, 230-1.
7. A. Kraus, *Farben-Ztg.*, 1932, 38, 322.
8. J. J. Fox and T. H. Howles, *Analysis of Pigments, Paints and Varnishes*, New York, 1927, p. 160.
9. H. A. Gardner, *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colours*, 5th ed., Washington, 1930.
10. A. W. van Heuckeroth, *Am. Paint and Varnish Mfrs.' Assoc.*, 1930, Circ 369, 354-417.
11. E. H. Huntress and S. P. Mulliken, *Identification of Pure Organic Compounds*, 1, New York, 1941.
12. R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, New York, 1940.
13. E. Hermann, *Peintures, Pigment, Vernis*, 1933, 10, 26 (analysis of albertols).
14. L. Kern, *Farbe u. Lack*, 1933, 534 (analysis of albertols).
15. H. Ulrich, *ibid.*, 1933, 318 (estimation of dicarboxylic acids in synthetic resins by insolubility in benzene).
16. W. Esch, *Kunststoffe*, 1938, 28, 226-7.
17. W. Esch and R. Nitsche, *Kunstharze u. a. plastische Massen*, 1938, 8, 240.
18. J. F. Thorpe and M. A. Whiteley, *A Student's Manual of Organic Chemical Analysis*, 1926, 51-2.
19. T. H. Durrans, *Solvents*, 4th ed., London (Chapman & Hall) 1938.
20. Distillers' Co. Ltd. and H. M. Stanley, Polystyrene compositions. B. P. 506,290.
21. B. F. Goodrich Co., Polyvinyl halide compositions, U.S.P. 2,193,613, 18 3 37.
22. W. H. Stevens, *Analyst*, 1931, 56, 528-9.
23. O. C. Ellington, *J.S.C.I.*, 1929, 48, 267 T.
24. J. Scheiber, *Farbe u. Lack*, 1933, 502.
25. D. Canneleter, *Verfkroneik*, 1934, 7, 256; B., 1934, 971.
26. F. Kramer, *Farben-Ztg.*, 1935, 40, 1142-3.
27. E. Storfer, *ibid.*, 1937, 42, 483.
28. C. P. A. Kappelmeler, *ibid.*, 1935, 40, 1141-2.
29. A. E. G. Brown, *Oil, Colour Trades J.*, 1936, 89, 1489.
30. A. Nielsen, *Paint Manuf*, 1936, 6, 153.
31. R. L. Jenkins, R. McCullough, and C. F. Booth, *Ind. Eng. Chem.*, 1930, 22, 31.
32. C. H. Penning, *ibid.*, 1930, 22, 1180.
33. F. Seeligmann and E. Zleke, *Handbuch der Lack- und Firnisfabrikation*, 4th ed., Berlin, 1930, p. 662.
34. H. Wolff, *Farbe u. Lack*, 1928, p. 85.
35. H. A. Gardner, *Am. Paint and Varnish Mfrs.' Assoc.*, 1928, Circ. 330.
36. A. E. Stauderman and H. L. Beakes, *Ind. Eng. Chem.* 1928, 20, 674.
37. V. H. Turkington, R. G. Shuey, and H. W. Butler, *ibid.*, 1930, 22, 1177.
38. *Brit. Plastics*, 1935, 7, 25, 72, 112, 214.
39. C. P. A. Kappelmeler, *Farben-Ztg.*, 1937, 42, 561.
40. P. Kampf, *Pharm. Arch. Helv.*, 1931, 6, 170.
41. *Syn. and Appl. Fin.*, 1933, 4, 112-13.
42. L. Metz, *Kunststoffe*, 1937, 27, 269.
43. P. G. Sandford, *Nitro-Explosives*, London, 1896, p. 212.
44. W. L. Barnett, *J.S.C.I.*, 1921, 40, 9 T.
45. E. G. Couzens, J. A. Eatherington and L. W. Turner, *Chemistry and Industry*, 1940, 209.
46. G. Kline, *Symposium on Plastics*, A.S.T.M., 1938; Appendix, p. 50.

47. W. D. Owen, *Brit. Plastics*, 1930, 2, 310.
48. W. Zebrowski, *Chemie und Technologie der Kunststoffe*, Leipzig (Academische Verlagsgesellschaft M.B.H.), 1939, p. 521 et seq.
49. *Ibid.*, p. 487.
50. H. Freundlich, *J.S.C.I.*, 1934, 53, 218 T.
51. G. W. Scott Blair, *Introduction to Industrial Rheology*, Philadelphia, 1938, p. 134.
52. R. Houwink, *Physikalische Eigenschaften und Feinbau von Natur- und Kunstharzen*, Leipzig, 1934.
53. R. Houwink, *Elasticity, Plasticity, and Structure of Matter*, Cambridge, 1937.
54. J. M. Burgers, *First Report on Viscosity and Plasticity*, *Academy of Sciences, Amsterdam*, 1935, p. 105.
55. G. W. Scott Blair and F. M. Coppen, *Nature*, 1940, 146, 840.
56. G. W. Scott Blair, *Introduction to Industrial Rheology*, Philadelphia, 1938, p. 22 et seq.
57. *Ibid.*, p. 70 et seq.
58. C. J. van Neuwenberg, *First Report on Viscosity and Plasticity*, Amsterdam, 1935, p. 143.
59. R. Houwink, *Elasticity, Plasticity and Structure of Matter*, Cambridge, 1937, p. 10.
60. I. Williams, *Ind. Eng. Chem.*, 1924, 16, 362.
61. J. R. Scott, *Trans. Inst. Rubb. Ind.*, 1931, 7, No. 2.
62. R. L. Peek, *J. Rheology*, 1932, 3, 345.
63. R. Houwink and P. N. Heinze, *Ind. Eng. Chem., Anal. Ed.*, 1938, 10, 680.
64. W. G. Wearmouth, *Chemistry and Industry*, 1938, 57, 1176-82.
65. W. G. Wearmouth and J. S. Small, *Brit. Plastics*, 1941, 144, 377.
66. G. W. Scott Blair and F. M. Coppen, *J. S. C. I.*, 1941, 60, 190 T.
67. W. G. Wearmouth and I. I. Behrenblatt, *Nature*, 1941, 148, 26.
68. R. Houwink, *Elasticity, Plasticity, and Structure of Matter*, Cambridge, 1937, pp. 7-9.
69. J. Delmonte, *Mod. Plastics*, May, 1940, 17, 49; June 1940, 17, 65.
70. W. M. Findley, *A.S.T.M. Reports*, June 1941, *Mod. Plastics*, Sept. 1941, 19, 57.
71. N. A. De Bruyne, *Proc. Phys. Soc.*, 1941, 53, 257.
72. E. N. da C. Andrade, *Nature*, 1930, 125, 309.
73. L. Hartshorn, N. J. N. Megson, and E. Rushton, *Proc. Phys. Soc.*, 1940, 52, 817.
74. F. Horst Muller, *Chemie und Technologie der Kunststoffe*, 1939, p. 117.
75. B.S.S. No. 771, Synthetic Resin (Phenolic), Moulding Materials and Mouldings.
76. B.S.S. No. 316, Synthetic Resin Varnish Paper Boards and Tubes.
77. B.E.S.A., Aircraft Specification, No. 2, I, 25, March 1929.
78. A. G. Batson and J. H. Hyde, *Mechanical Testing*, vol 1, p. 113. London (Chapman & Hall), 1931.
79. H. D. Owen, *Brit. Plastics*, 1931, 2, 514 et seq.
80. H. M. Richardson, *Symposium on Plastics*, A.S.T.M., 1938, p. 9 et seq.
81. W. D. Owen, *Brit. Plastics*, 1931, 2, 350.
82. W. F. Bartoc, *Mod. Plastics*, March, 1940, 17, p. 47.
83. A. V. H. Mory, *Ind. Eng. Chem.*, 1927, 19, 1108.
84. A.S.T.M., D 48-37, Moulded materials used for electric insulation.
85. E.R.A., A/510, Non-ignitable boards and mouldings.
86. E.R.A., A/56, Laminated sheet materials.
87. A.S.T.M., D. 229-28 T, Laminated sheet materials.
88. W. Rohrs, *Kunststoffe*, 1936, 26, 47.
89. H. Chase, *Brit. Plastics*, 1932, 4, 108.
90. W. D. Owen, *Brit. Plastics*, 1931, 2, 556.
91. V.D.E., 318.0302.
92. R. Nitsche and E. Salewski, *Kunststoffe*, 1939, 29, 209.
93. E.R.A., Rept. Ref. B/52, *J.I.E.E.*, May, 1922.
94. W. D. Owen, *Brit. Plastics*, 1935, 7, 137.
95. *Ibid.*, 1935, 7, 259.
96. H. Chase, *Brit. Plastics*, 1932, 4, 155.
97. J. Schelber and K. Sändig, *Artificial Resins*, London (Pitman), 1931.
98. A.S.T.M., D. 256-34 T.
99. L. I. Hopkins, *Mod. Plastics*, Oct., 1935, 13, 17.
100. H. Burns and W. W. Werring, *Mod. Plastics*, Aug., 1937, 15, 37.
101. J. H. Lavery and I. V. Southwell, 1934, Selected Engineering Papers No. 142, The Institute of Civil Engineers.
102. E. H. Warlow-Davies and R. V. Southwell, *The Correlation of Impact Tests and the Problem of Standardization*, Dec. 1936. The Institute of Mechanical Engineers.
103. B. Andersen, *Mod. Plastics*, Oct., 1937, 15, 20-1.
104. S. L. Bass and T. A. Kauppl, *Ind. Eng. Chem.*, 1937, 29, 678.
105. J. C. Pitzer, A.S.T.M., *Symposium on Plastics*, 1938, p. 31.
106. W. D. Owen, *Brit. Plastics*, 1931, 2, 565.
107. H. O'Neill, *The Hardness of Metals and its Measurement*, London (Chapman & Hall) 1934
108. S. M. Petrenko, W. Ramberg, and B. Wilson, *Bureau Standards J. Research*, 1930, 17, 61.
109. A.S.T.M. 1934, D.229-34 T, vol. 34, Part 1, p. 1055.
110. G. M. Kilne and B. M. Axilrod, *J. Ind. Eng. Chem.*, 1936, 28, 1170.
111. *Brit. Plastics Year Book*, 1940, p. 456.
112. S. R. Williams, *Hardness and Hardness Measurements, Instruments*, 1937, 10, Nos. 1-9.
113. C. Bierbaum, *Metal Progress*, 1930, 18, 42.
114. H. Chase, *Brit. Plastics*, 1933, 4, 338.
115. S. E. Sheppard and J. J. Schmitt, *J. Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 302.
116. G. Sward, U.S.P. 1,935,752, Nov. 21, 1933.
117. H. A. Gardner, *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colours*, Washington, 6th ed. 1930.
118. W. Zebrowski, *Chemie und Technologie der Kunststoffe*, Leipzig, 1930, p. 540.
119. A.S.T.M. D. 48-37, 1937, Supplement to book of A.S.T.M. Standards, p. 232.
120. W. D. Owen, *Brit. Plastics*, 7, 1936, May, p. 552.

121. W. D. Owen, *Electrical Times*, 1938, p. 931.
122. W. D. Owen, *Brit. Plastics*, 1932, July, p. 58.
123. A.S.T.M., D. 5-26.
124. A.S.T.M., D. 86-28.
125. *Brit. Plastics*, 1934, 6, p. 54.
126. M. Forrer, *Brit. Plastics Year Book*, 1933, p. 68.
127. M. Krahl, *Elektrotechn. Z.*, 1931, 52, 439.
128. U.S.P. 2,066,016 (1936).
129. C. H. Penning and L. W. A. Meyer, *Brit. Plastics* 1938, 10, 191-2, 195-6.
130. C. H. Penning, A.S.T.M. *Symp.*, 1938.
131. A.S.T.M. Tentative method of test for measuring flow temperature of thermoplastic materials, D. 569-40 T.
132. L. W. A. Meyer, *Mod. Plastics*, Dec., 1940, 18, p. 59.
133. J. H. Dillon and N. Johnson, *Physics*, 1933, 4, 225.
134. M. Krahl, *Kunststoff-Technik*, 1930, 9, 204.
135. A. Schmittmann, *Kunststoffe*, 1930, 29, 190.
136. K. Brandenburger, *ibid.*, 1936, 26, 126.
137. C. J. van Nieuwenberg, *2nd Rept. on Viscosity and Plasticity*, Academy of Sciences, Amsterdam, 1938, p. 241.
138. E. Karrer, *J. Ind. Eng. Chem.*, 1920, 21, p. 770; 1929 (Anal. Ed., vol. 1, 158).
139. *Kunststoffe*, 1937, 27, 255-6.
140. M. Speitman, *Brit. Plastics*, 1930, 10, 447.
141. Burns and Hopkins, *Modern Plastics*, Aug. 1937, 14, p. 42.
142. N. A. De Bruyne, Aero Research, Ltd., Duxford, *The Aeroplane*, 1936, Feb 19th
143. British Standard Specification for Aircraft Material, F. 56.
144. W. E. Gloor, *Modern Plastics*, April, 1940, 18, 63.
145. A.S.T.M. Tentative method of test for water absorption of plastics, D. 570-40 T, 1940.
146. C. R. Fordyce and L. W. A. Meyer, *Ind. Eng. Chem.*, 1940, 32, 1053.
147. V D. E., 0305 (1932).
148. W. Schramm and W. Zebrowski, *Elektrotechn. Z.*, 1928, 49, 601.
149. B.S.S. 737, 1937. Non-ignitable and self-extinguishing boards for electrical purposes. B.S.S., 738, 1937. Non-ignitable and self-extinguishing properties of electric insulating materials.
150. A.S.T.M., Flammability D. 568-40 T, *Mod. Plastics*, April 1941, p. 62. A.S.T.M., D. 229-37 T, section 52-6. A.S.T.M., Book of Standards, 1937, p. 415.
151. W. D. Owen, *Brit. Plastics*, 1932, 4, 58.
152. W. O. Zinzow, A.S.T.M. *Symposium on Plastics*, 1938, p. 15.
153. A.S.T.M., D. 325-31 T. A.S.T.M., Tentative Test Standards, p. 1140.
154. G. M. Kline, A S T M. *Symposium on Plastics*, 1938, p. 35.
155. H. A. Gardner, *Sun-Spray Rapid Test-ruck*, Clrc. No. 534, Nat. Paint, Varnish, and Lacquer Association, June, 1937, p. 177.
156. B. M. Axilrod and G. M. Kline, A Study of Transparent Plastics for Use in Aircraft. *J. of Research, Nat. Bur. Stand.* 19, Oct. 1937, pp. 367-400.
157. B.S.S. 757, 1937.
158. M.A.P. Specification D.T.D., 402.
159. M. E. Fogle, *Trans. Illum. Eng. Soc.*, 1936, 31, 773.
160. *Nat. Bur. of Standards*, 19, No. 4, Oct. 1937.
161. *Mod. Plastics*, Jan. 1937, 14.
162. B.S.S. 188, 1937. Determination of viscosity of liquids in absolute (C.G.S.) units.
163. F. D. Farrow, *J. Chem. Soc.*, 1912, 101, 347.
164. O. Scarpa, *Gazz. chim. ital.* 1910, II, 261; *J.S.C.I.*, 1911, 30, 51.
165. Guy Barr, Aeronautical Research Committee Reports, Memorandum No. 988. (M 31). 1926.
166. W. H. Gibson and L. M. Jacobs, *J. Chem. Soc.*, 1920, 117, 473.
167. L. Archbutt and R. M. Deeley, *Lubrication and Lubricants*, 5th ed., London 1927.
168. Guy Barr, *A Monograph of Viscometry*, Oxford, 1931.
169. H. Mark, *Physical Chemistry of High Polymeric Systems*. New York, 1941, vol. 2, pp. 258-95.
170. E. G. Couzens and W. G. Wearmouth, *J.S.C.I.*, 1942, 61, 69-74.
171. *Nature*, 1942, 149, 702.

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