ELSEVIER'S POLYMER SERIES

ELSEVIER'S POLYMER SERIES

ON THE CHEMISTRY, PHYSICS, AND TECHNOLOGY OF HIGH POLYMERIC AND ALLIED SUBSTANCES

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Fundamentals of

SYNTHETIC POLYMER
TECHNOLOGY

IN ITS CHEMICAL AND

PHYSICAL ASPECTS

by

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PREFACE

Some books have already been published on the Technology of Synthetic Polymers. None of these, in the author's opinion, has stressed the *basic principles* of this important subject sufficiently to enable the reader to understand its technological aspects and to interpret the results of tests and the properties of the final products in the light of those basic principles.

That is what the author has set out to do in this book. The principle on which the book is planned has necessitated devoting a good deal of space to theoretical and general matters, bringing it on a higher scientific level than most other books on polymer technology and trying to make it especially suitable for university students.

A feature peculiar to this book, as distinct from most others on the subject, is an endeavour to give the views and methods prevailing in the three chief centres of polymer research, namely, North America, Great Britain, and the Continent of Europe.

The first edition of this book appeared under the title: Technology of Synthetic Polymers. This title has been changed, since it is desirable to express more clearly that its purpose is to stress the fundamental background of polymer technology and to avoid entering into minor details.

The second edition comprises a very great number of alterations compared with the first one; moreover, it has been considerably enlarged and brought up to date.

The author's thanks are due to Mr. N. G. BISSET for his careful correction of the English language.

WASSENAAR (Netherlands), Spring 1948

R. HOUWINK

CONTENTS

CHAPTER I

THE CHEMISTRY OF POLYMERS

§ 1. INTRODUCTION

We have to thank STAUDINGER [1] for creating the important concept of macromolecules, which has taken us so much farther.

It is impossible however to define exactly what is called a macromolecule. There is a tendency to speak of macromolecular materials when the molecules comprise more than 1000 atoms; from Table 1 it appears that this limit is much too low.

An upper limit cannot be given either, since a diamond crystal, containing primary bonds only, can be conceived as a single macromolecule.

There exist different systems of classifying the macromolecules, according to their size. The classification introduced by STAUDINGER [2] for chain molecules is as follows:

TABLE 1.

CLASSIFICATION OF CHAIN MOLECULES ACCORDING TO THEIR SIZE

Designation:	Number of structural units
Low molecular products	< 50
Hemicolloids	50—500
Mesocolloids	500—2500
Eucolloids (macromolecular)	> 2500

The mesocolloids form, in this system, the transition to the macromolecular materials proper.

§ 2. POLYMERIZATIONS AND CONDENSATIONS [3]

There are two ways of building up high molecular substances. The first one is by *addition*, in which no products are eliminated during the process.

[1] H. STAUDINGER, Helv. Chim. Acta, 5 (1922) 785.
[2] H. STAUDINGER, Trans. Faraday Soc., 32 (1936) 97.
[3] For a survey: H. MARK in R. E. BURK and O. GRUMMITT, The Chemistry of Large Molecules, New York 1943, p. 1; H. MARK and R. RAFF, High Polymeric Reactions, New York 1941.

of formation. This type of process is already known from classical organic chemistry, but in the field of polymers a special kind has become important, namely the *addition polymerization*, which is usually simply called *polymeri-zation*. An example of this is found in the polymerization of styrene according to Fig. 1.
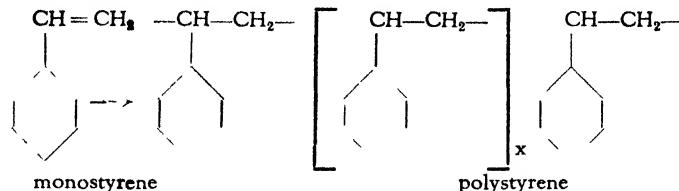
Fig. 1.   The polymerization of styrene.

When, on the other hand, products, like water, are formed besides the main product we speak of a *condensation* and Fig. 2 shows how p-cresol can combine with formaldehyde by such a reaction. The essential difference be-tween the polymerizations and the condensations is, that the latter are irre-versible equilibrium reactions. Their progression is dependent on the removal of the by-products, e.g., by vacuum distillation, which is not true for polymerizations. These are chain-reactions; as soon as they have been initiated, they proceed by themselves.
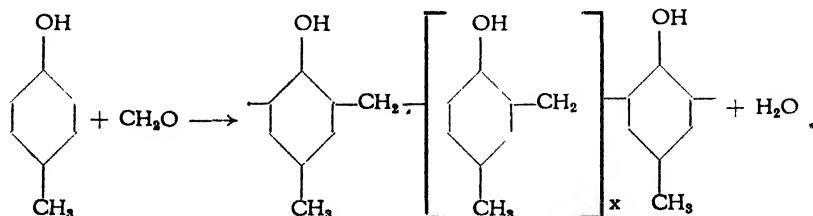
Fig. 2.   Condensation reaction of p-cresol and formaldehyde.

a.   *Polymerizations.*

When considering the formation of polystyrene as an example, one assumes that the reaction takes place in stages, as in Fig. 3; we speak here of a chain-reaction.

1. *Start reaction.* First of all, the monomer molecule is activated, a styrene

I. Styrene   II. Activated styrene   III. Polystyrene macroradical
                     (styrene radical)

$$CH_2—CH_2—\left[\,CH—CH_2\,\right]_x\ —C=CH_2$$

Stop reaction ⟶
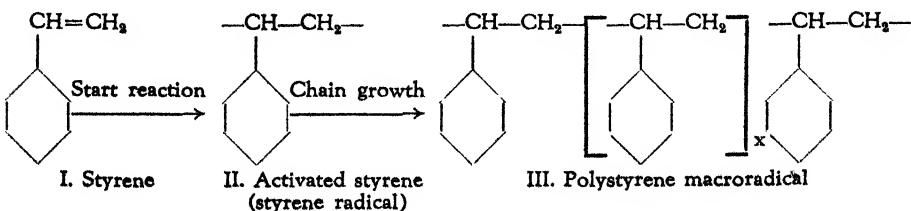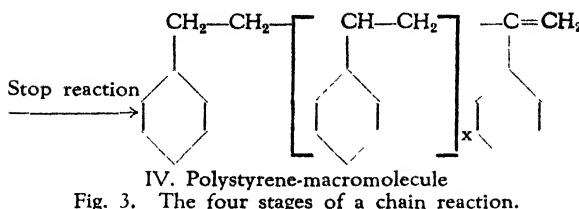
IV. Polystyrene-macromolecule
Fig. 3. The four stages of a chain reaction.

radical being formed. This reaction. which is called the primary process, the *start reaction*, the nuclei formation or the activation reaction, is generally endothermic and, for styrene, has an activation energy of 23.5 kcal per mole (Table 2).

In Fig. 3 the activation is represented by the opening of the double bonds. This means that by concentration of a great deal of energy e.g., in consequence of the absorption of light, certain monomers become active nuclei; they possess unshared electrons. It is clear that in this way they are enabled to add a new monomer, thereby forming a new radical. Such processes are extremely sensitive towards certain catalysts, the mechanism of which will be discussed on p. 5

TABLE 2.

ACTIVATION ENERGY OF THE START REACTION

Substance	Temperature range in °C.	Activation energy in kcal/mole
Styrene	80—131	23.5
Vinyl acetate (pure)	82—110	23.1
Vinyl acetate (in toluene)	82—111	22.3
Methacrylic acid ester	100—210	10.3

2. *Chain growth.* Under the influence of the activated nuclei other monomers become activated and the opportunity now exists for the mutual sharing of the electrons, that means: the formation of an atomic bond. The existing energy then is available again so that by successive addition of several monomers a molecular chain is formed. During this reaction *macroradicals*, as represented in Fig. 3, continue to exist. The progress of this growth reaction is very rapid as compared to that of the start reaction, so that when occasionally a radical is formed it grows immediately into a macroradical with a final length, controlled by the stop reaction (see below).

3. *Stop reaction.* By means of this *stop reaction* the macroradical becomes a *macromolecule*. In Fig. 3 the cause of this is supposed to be the migration

of an H atom; however, other explanations are possible, e.g., by ring-formation
or by the reaction with impurities (O_2). It is also sometimes presumed that
the macroradical, whilst transmitting the energy, activates a monomeric
molecule into a radical, but that occasionally the macroradical itself
becomes converted into a macromolecule.

There have been many discussions whether or not it is necessary to suppose
the occurrence of a stop reaction. The opinion is sometimes held that the
tendency of the growing chains to add as much monomer as possible would
limit the length of the chain, because at a certain moment no more monomer
would be available. To this idea it can be objected that it has been proved
experimentally that the chains, as soon as formed, receive their definite length.
In consequence of the stop reaction not all chains have an equal length;
there is obtained a polydisperse mixture, which we shall consider
again on p. 8.

4. *Polymerization rate.* The rate of the total reaction is controlled by the
combination of the three above-mentioned partial processes. In practice, the
start reaction and the stop reaction are usually the decisive mechanisms;
whether or not chain growth can take place is decided by these factors.
Because the primary process is the slower one, its velocity V_A is immediately
obtained from (1), each start reaction corresponding to the formation of one
macromolecule.

$$V_A = \frac{V_{Br}}{P} \quad \dots \dots \dots \dots \dots \dots \dots (1)$$

in which V_{Br} = velocity of the brutto reaction, P = mean degree of poly-
merization.

We know catalysts which accelerate certain partial reactions; we also know
inhibitors which can retard them and in these ways the reaction process
can be influenced (see below).

As is known already from classical chemistry, the rate of reaction of an
unsaturated substance is strongly influenced by the type and the exact place
of the double-bonds in the molecule. This is shown by Table 3, in which is
indicated the time in which one half of the monomer is converted into
polymer.

TABLE 3.

INFLUENCE OF THE UNSATURATION ON THE POLYMERIZATION-VELOCITY

Monomer	Formula	Time to convert half of the monomer
Diacetylene	$CH \equiv C - C \equiv CH$	minutes at 0° C.
Divinylacetylene	$CH_2 = CH - C \equiv C - CH = CH_2$	minutes at 50° C.
Vinylacetylene	$CH_2 = CH - C \equiv CH$	hours at 50° C.
Acetylene	$CH \equiv CH$	— — —
Vinyl compounds	$CH_2 = CH - R$ . . . . ($R = C_6H_5$, Cl, OH, OCO—CH_3, COOH, COOR, CN)	hours at 100° C.
Butadiene	$CH_2 = CH - CH = CH_2$	weeks at 100° C.
1.5-Hexadiene	$CH_2 = CH - CH_2 - CH_2 - CH = CH_2$ . . .	hours at 250° C.
1-Butene	$CH_3 = CH - CH_2 - CH_3$	days at 500° C.
Ethylene	$CH_2 = CH_2$	stable up to 700° C.

It is obvious that a rise in temperature increases the reaction rate; other factors influencing the reaction are the nature and the concentration of the solvent.

We have pointed out already the important role of the *catalysts* such as peroxides (e.g., benzoyl peroxide), and also $SnCl_4$.

Their action can take place in three different ways, viz:

a. They form radicals by themselves, which are built in in the macromolecules [1].

b. Catalysts like BF_3 and $AlCl_3$, which have a deficit in their electron octet, exert a polarizing effect on the double bond of the monomer. This activated monomer can directly polarize other monomers or it can do so after being added to the catalyst (Fig. 4).

$$F: B \overset{\leftarrow}{\underset{\uparrow}{+}} \overset{R}{\underset{|}{CH}} = CH \rightarrow F: \overset{..}{B}: \overset{R}{\underset{|}{CH}} - CH_2 \rightarrow F: \overset{..}{B}: \overset{R}{\underset{|}{CH}} - CH_2: \overset{R}{\underset{|}{CH}} - CH_2 \rightarrow etc.$$

F deficit   F (—) (+)   F (—) (+) (—) (+)
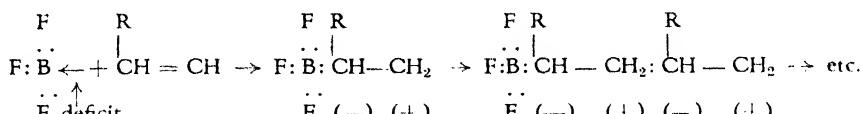
Fig. 4.   Catalytic action of BF_3 on polymerization.

c. In the case of polymerization of diolefins by alkali metals, the latter are donors of electrons, leading to negative bivalent ions. These possess lone pairs of electrons, which can polarize and subsequently add other

$$CH_2 = CH - CH = CH_2 + 2 Na \rightarrow \left[:CH_2 - CH = CH - CH_2: \right]^{(-)} \ ^{(-)} + Na_2^{+ +} \rightarrow$$

$$:CH_2^{(-)} - CH = CH - CH_2 - CH_2 - CH = CH - CH_2 - CH_2 - CH = CH - CH_2:^{(-)} \rightarrow etc.$$

Na+   Na+
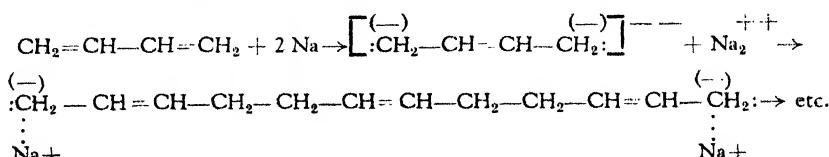
Fig. 5.   Catalytic action of sodium on butadiene polymerization.

[1] See e.g. F.O. Rice and D.V. SICKMAN, *J. Am. Chem. Soc.*, 57 (1935) 1384.

butadiene monomers (Fig. 5). The Na-ions are each time removed to the negative end of the growing particle. Since butadiene can also be polarized like this:

$$\underset{:\ CH_2\!-\!\overset{}{CH}\!-\!CH\!=\!CH_2\ ,}{\overset{(-)\quad\ (+)}{}}$$
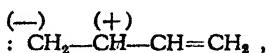
the capacity of forming branches can be understood (1:2 and 1:4 reactions, see p. 15).

5. Inhibitors.

As an example of an *inhibitor* we may point to oxygen in the photopolymerization of vinyl compounds. It is remarkable that in dark oxygen is known to have a pronounced accelerating effect, but in ultraviolet light a preferential action between the monomer and oxygen takes place, leading to a peroxide. In this case three possible reactions are suggested [1] to take place, of which no. 2 is preferred; that means: active nuclei are deactivated.

$$
\begin{aligned}
&1. \quad M + UVL \longrightarrow M^x \\
&2. \quad M^x + O_2 \longrightarrow MO_2 \text{ (preferred reaction)} \\
&3. \quad M^x + M \longrightarrow M + MM^x, \text{ etc.,} \\
&\qquad \text{where } M = \text{unactivated monomer} \\
&\qquad\qquad\quad M^x = \text{active centre} \\
&\qquad\qquad\quad MO_2 = \text{peroxide.}
\end{aligned}
$$

6. Modifiers.

A further very important point in polymerization is whether only linear chain growth takes place or whether branching also can occur. An example of this can be found in the 1:2 polymerization of butadiene, next to 1:4 polymerization. Fig. 6a shows how butadiene (and in general a diene) can form linear molecules by means of 1:4 addition only.

$$
\begin{array}{ccccccc}
1 & 2 & 3 & 4 & & 1 & 2 \\
\ldots-C-C=C-C-\ldots & & \ldots-C-C-\ldots \\
& & & & & & | \\
& & & & & & C\ 3 \\
& & & & & & || \\
& & & & & & C\ 4
\end{array}
$$
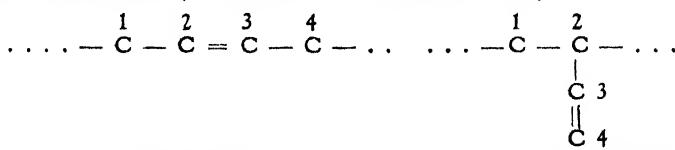
a) 1:4 polymerization.   b) 1:2 polymerization.
Fig. 6.   1:2 and 1:4 polymerization.

If, however, 1:2 polymerization according to Fig. 6b occurs, a double bond is left available at C-atom number 4, which is capable of further addition, leading to net building. In this way insoluble polymers come into being. In order to prevent this as much as possible, *modifiers or regulators*, are added, catalysing 1:4 addition and inhibiting 1:2 addition. Mercaptans, for example, are used for this purpose.

[1] C. E. BARNES, J. Am. Chem. Soc. 67 (1945) 217.

b. Condensations (Equilibrium reactions).

During condensation reactions, a fundamentally different course is followed, the degree of polymerization of the molecules formed depending on an equilibrium. Let us take for example the formation of a polyester from glycol and a dicarboxylic acid according to the example below. The ester, which is first formed, can only continue to react, when the reaction water is removed.

$$
\begin{array}{ccccc}
\text{OH} & \text{OH} & \text{COOH} & \text{COOH} & \\
| & | & | & | & \\
\text{CH}_2 & \!\!-\!\text{CH}_2 + \text{CH}_2 & -\! & \text{CH}_2 &
\end{array}
\longrightarrow
\begin{array}{ccc}
\text{OH} & \text{O} & \text{COOH} \\
| & \| & | \\
\text{CH}_2\!-\!\text{CH}_2\!-\!\text{O}\!-\!\text{C}\!-\!\text{CH}_2\!-\!\text{CH}_2 &
\end{array}
+ \text{H}_2\text{O}
$$

Esterification of glycol with a dicarboxylic acid.
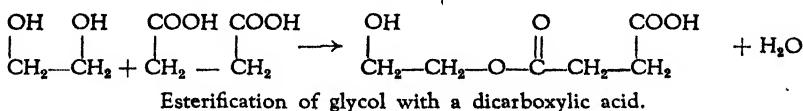
The following equation then can be used:

$$
\frac{C\,\text{ester} \quad . \quad C\,\text{water}}{C\,\text{acid} \quad . \quad C\,\text{alcohol}} = K \dots\dots\dots\dots\dots\dots\dots (2)
$$

Here C indicates the concentrations. Unlike the polymerizations there is no

a) Polymerization of styrene   b) Condensation of a polyester
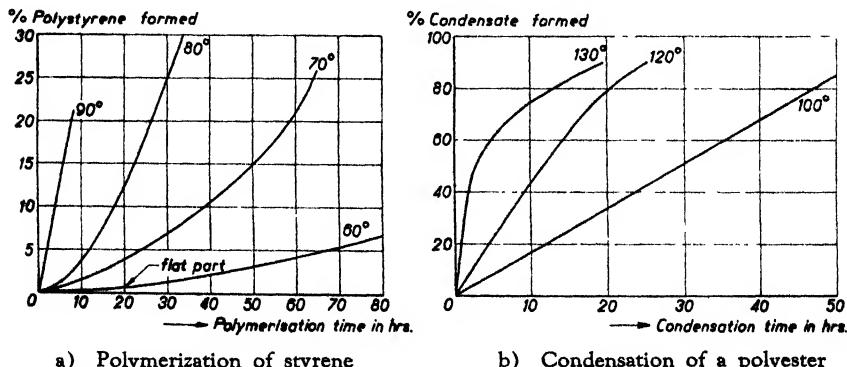
Fig. 7. During polymerization the reaction has an induction period, but afterwards pursues its course faster and faster. In the condensation reaction the situation is just the opposite.

question here of processes, which take a spontaneous course; the GULDBERG-WAAGE law, well-known from classical chemistry, is applicable. On account of the development of the condensation-equilibrium, it is very difficult to attain the high molecular weights which one obtains in the polymerization. Technically this problem is usually rendered very difficult on account of the distance the water must travel through the tough high molecular mass. Fig. 7 shows the fundamentally different course of the two sorts of reactions. During the polymerization, especially at the lower temperatures, the induction period (the flat portion of the curve) can be recognized: that is the period of the start-reaction. Then the reaction rate goes up rapidly (chain growth). On the contrary, in the condensation (Fig. 7b), the reaction starts rapidly, but then gradually slows down as a result of the equilibrium setting in.

§ 3. THE MOLECULAR SIZE AND ITS DISTRIBUTION.

We have mentioned on p. 4 that all the molecules do not usually acquire the same length, depending on the circumstances of reaction. In nature this is also encountered; Table 4 shows the molecular size of some important natural and technical substances. For many practical considerations it is

TABLE 4.

MOLECULAR SIZE OF SOME POLYMERS [1]

Substance	Mol. Weight	Polymeriz. Degree
Cellulose (wood)	300,000—500,000	2,000—3,000
Cellulose, regenerated (rayon)	75,000—100,000	500— 600
Rubber (native)	150,000—200,000	2,000—3,000
Polystyrene (for moulding)	60,000—500,000	1,200—6,000
Polystyrene (for coating)	80,000—120,000	800—1,200
Nylon	16,000— 32,000	150— 300

sufficient to study the average molecular weight of a certain polymer, but in other cases it is necessary to know exactly the distribution function of the molecular size. We show in Fig. 8 for three different materials this distribution function according to the weight in grams (W) and also according to the number (n) of gram-molecules, which for every fraction exist in one gram of the material involved [2].

In polyisobutylene the small molecules are most frequent.

The curve for nitrocellulose is of an entirely different character; here the large molecules with a polymerization degree of 700 are the most numerous. As the course of this curve probably depends on the constitution of the cellu-

a. Polyisobutylene b. Nitrocellulose c. Phenol-for-maldehyde resin (estimated)
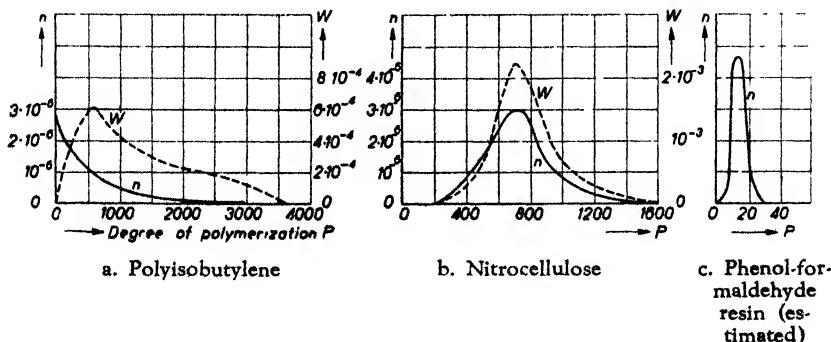
Fig. 8. Distribution-curves of the polymerization degree P according to weight (w) and number (n) for different polymers.

[1] H. MARK, Am. Scientist, 31 (1943) 104.
[2] G. V. SCHULZ, Z. physik. Chem., B 30 (1935) 379; B 32 (1936) 27.

lose molecules, the question comes up whether perhaps the distribution is similarly regular for all natural materials. If this were true, we might conclude immediately that Nature constructs its chains in an entirely different manner than is done in technical practice.

For the low molecular condensation products of the type of phenol-for-maldehyde resins in the A-state we may probably expect a distribution curve according to Fig. 8c, which is characterized by the fact, that only small mole-cules occur which do not vary much in their dimensions.
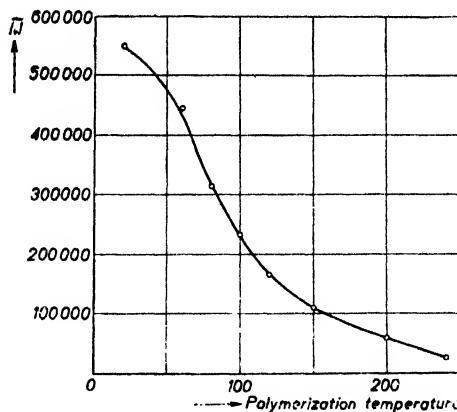

Fig. 9.   Decrease of the molecular weight with increasing polymerization temperature.

The distribution curves can be calculated from the velocity constants of the polymerization reaction; this shows to what extent we are now capable of controlling the course of such processes.

Naturally, the length of the chains which are formed depends to a great extent on the polymerization temperature, as is shown by Fig. 9, the ratio of V_A to V_{Br} in equation (1), page 4, being influenced by the temperature

§ 4.   BULK, SOLUTION, AND EMULSION POLYMERIZATION [1]

Polymerizations and condensations can be carried out in three different ways, according to the degree of dispersion. We speak of *bulk polymerization* when the reaction takes place in a solid state without diluents, and of *solution polymerization* or *emulsion polymerization* accordingly as the monomer is in solution or in emulsion. There is evidence that *suspension or pearl polymerization*

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[1]   See for a summary: W. P. HOHENSTEIN and H. MARK, *J. Polymer Sci.*, 1 (1946) 127, 549.

may be distinguished where the polymerization occurs chiefly within the drops of monomer (in the emulsion polymerization it seems to occur in the dispersing agent).

In *bulk polymerization* one starts from the liquid monomer, which changes gradually into the solid polymer. Technically, such a process is impracticable, as during the course of the reaction one cannot stir the ever toughening material, so that it is impossible to maintain a correct distribution of temperature.

Solution polymerization avoids this difficulty, but it usually leads only to low degrees of polymerization. Moreover, it is very difficult to remove the solvent afterwards and the process is expensive.

Emulsion polymerization is the favourite method. The (more or less soluble) monomer is emulsified by means of a soap, mixed with catalysts, and heated. When the reaction is finished, an artificial latex has been formed which can be used as such or from which the polymerizate is obtained by means of coagulation or evaporation.

An average example of an emulsion polymerization is the following:

TABLE 5.

RECIPE FOR EMULSION POLYMERIZATION

Water	60—80%
Monomer	40—20%
Emulsifier	0.1— 4% on monomer
Catalyst	0.1— 1% „ „
Protective colloid and modifier.	

The role of the protective colloid is to prevent premature coagulation; the modifier serves to control the molecular weight.

It is not yet known with certainty, at which point polymerization takes place. There is much evidence[1], that nucleus formation partly starts in the monomer, entrapped in the soap micelles (Fig. 10). With the aid of X-rays it has been shown that in the case of styrene the inclusion of monomer increases the size of the soap micelle from 40 Å to 50 Å. Another locus of nucleus formation seems to be in the water phase, the dispersed monomer molecules becoming activated. These activated nuclei migrate into the soap micelles, giving rise to polymerization. It may be suggested that due to absorption of more and more monomer these micelles grow into droplets, gathering new soap molecules from other micelles on their surface.

Initially, these droplets will contain a mixture of monomer and polymer dissolved in each other, which in time is converted into polymer only.

[1] See for a summary: W. D. HARKINS, J. Am. Chem. Soc.. 69 (1947) 1428.
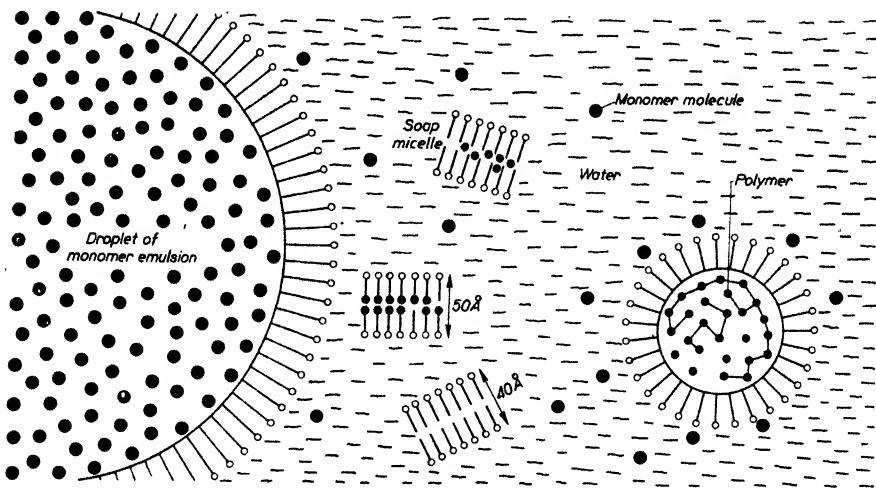
Fig. 10. Mechanism of the emulsion polymerization.

These suppositions are based on the following observations:

a. The diameter of the final polymer droplet is much smaller (say 1/1000) than that of the original monomer droplets.

b. By microscopic examination the monomer droplets can be seen to decrease during polymerization; usually, they disappear completely.

The decrease in size of the droplets is represented in Figure 11 for some emulsions [1]. It appears, that during the inhibition period the radius remains constant; it starts to decrease from the moment the conversion of monomer into polymer sets in.

The monomer drops seem to act as storehouses only, from which the molecules diffuse into the aqueous phase, and where they are trapped by soap micelles and polymer particles, polymerizing in both of these. In the case of styrene the rate of polymerization is much smaller than that of migration and the
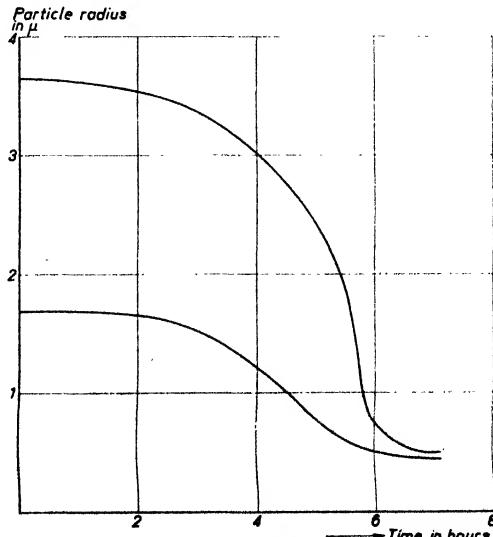

Fig. 11. Decrease of particle size during emulsion polymerization.

[1] W. P. HOHENSTEIN and H. MARK, J. Polymer Sci., 1 (1946) 127, 549.

over-all rate is thus controlled by the polymerization reaction. This means that the monomer concentration is constant throughout the polymerization process.

In the *suspension* or *pearl* polymerization the reaction seems to take place in the monomer droplets, the catalyst being soluble in the monomer and not in the water phase. The size of the polymer droplets remains equal to that of the monomer droplets; it can be adjusted by an adequate stirring process. Stabilizers are added in order to prevent the particles from coalescing; this stabilizer is simply washed out after completion of the polymerization. Then a simple drying operation follows and the product is obtained in the form of pearls. The course of the reaction is essentially the same as in bulk polymerization, the difference being that the reaction-place is subdivided in small parts (the individual droplets).

The fundamental advantage of emulsion polymerization (and also pearl polymerization) compared with block polymerization is, that the viscosity of the system does not change during the reaction, the viscosity of a dispersion of globules being independent of the contents or the magnitude of the droplets (see EINSTEIN equation (13), p. 55).

Stirring can therefore be carried out during the entire reaction and the heat developed can be carried away. This enables a quick reaction to take place, because the reaction temperature can be adjusted exactly without danger of having the temperature rise more in the centre of the material than in other parts—as in bulk polymerization. This also guarantees an equal molecular weight throughout the material; the molecular weight being dependent on the reaction temperature (see Figure 9, page 9).

§ 5.   COPOLYMERS.

Besides the so-called homogeneous polymers already mentioned, the *copolymers* — whose macromolecules are built up by two or more kinds of monomers — are also known. An example is the polyvinyl chloride-alcohol (Fig. 12), in which the chloride:alcohol ratio can be varied, e.g., 1:1 in this particular case. There is evidence, that the ability of the different monomers to donate or accept electrons is an important regulating factor in copolymerization [1].

$$\begin{array}{cccccccc}
H & H_2 & H & H_2 & H & H_2 & H & H_2 \\
-C & -C & -C & -C & -C & -C & -C & -C- \\
Cl & & OH & & Cl & & OH &
\end{array}$$

vinyl   vinyl
chloride   alcohol
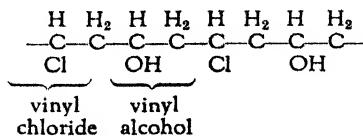
Fig. 12.   Example of a copolymer.

[1] C. C. PRICE, *J. Polymer Sci.*, 1 (1946) 83.

Especially in synthetic rubbers, we shall often encounter copolymers. They are usually formed by combined polymerization of two different monomers. However, it also happens that a combination which in itself is polymerizable reacts with a combination which in itself is not polymerizable (but unsaturated). Then, so-called *heteropolymers* are formed (see Figure 13).
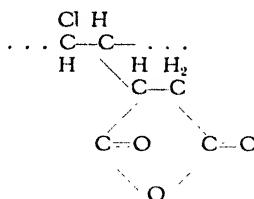

Fig. 13.   Vinyl chloride-maleic acid anhydride as an example of a heteropolymer.

§ 6.   IRREGULARITIES IN THE POLYMERIZED MOLECULES

We will see later on that from a technical point of view it is extremely important to know whether or not the macromolecules are simple regular chains, because this controls the capacity of crystallization. There are various irregular cases, however; we will discuss the most important of these.

a) When the monomer itself is asymmetrical, the head of one monomer may be attached to the tail of another (Fig. 14α). As long as this goes on according to the same pattern, the macromolecule is still regular, but example β) shows that an alternation of head-to-head and tail-to-tail configurations
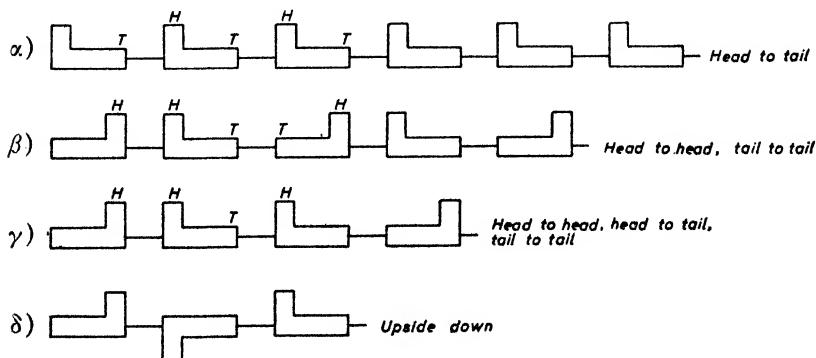

Fig. 14.   Regular and irregular macromolecules.

[1] W. L. SEMON, *Chem. Eng. News*, 24 (1946) 2900.

is also possible. In example γ) the molecule is also irregular, three types of arrangements being possible in the polymer. According to the laws of probability, it is evident that a completely irregular chain is most likely to be formed. Fig. 15 demonstrates this for an example in actual practice.

$$
CH_2=CHR
\begin{cases}
\nearrow \quad \underset{\text{head to tail}}{CH_2-\overset{R}{\underset{|}{CH}}-CH_2-\overset{R}{\underset{|}{CH}}-} \\
\longrightarrow \underset{\text{head to head}}{CH_2-\overset{R}{\underset{|}{CH}}-\overset{R}{\underset{|}{CH}}-CH_2-} \\
\searrow \underset{\text{random}}{CH_2-\overset{R}{\underset{|}{CH}}-CH_2-\overset{R}{\underset{|}{CH}}-\overset{R}{\underset{|}{CH}}-CH_2-}
\end{cases}
$$
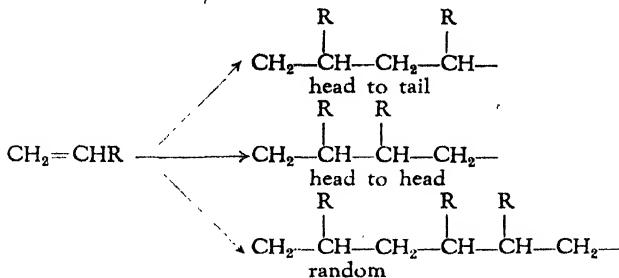
Fig. 15.   Three different arrangements in vinyl polymerization.

b) Considering also the possibility that certain monomer groups are arranged upside down — case δ — and combining this with γ), the probability of irregularity further increases.

c) Another complication arising in copolymerization is that in addition to having component B arrange itself head to tail and upside down with regard to component A, a certain part of the chain may be constituted —A —A—B—B—, whereas another part is constituted —A—B—A—B—.

d) In copolymerization the ratio $\dfrac{B}{A}$ in the chain often has proved to be different at the beginning of the reaction than at the end. This means that the polymer molecules initially formed are richer (or poorer) in A than those formed at the end of the reaction. This is clearly demonstrated in Fig. 16, where even the ratio $\dfrac{A}{B}$ appears to change in a different way depending on the constitution of the initial mixture. This proves that a constant ratio can only be obtained from a definite initial mixture of the components.

e) Another disturbing factor is that in many polymerizations the formation of cross-links can alternate with linear chain-growth; an example of this is the alternation of 1:2 addition with 1:4 addition. This important disturbing factor will be discussed in greater detail on p. 131, in connection with synthetic rubbers.

f) Chain-branching can occur because of a transfer of H-atoms from a methylene group to a radical. This leads to a radical on the chain where branching can occur (Fig. 17).

g) A final factor influencing the composition of synthetic polymers is the change in molecular weight during polymerization as shown [1] in Fig. 18. Especially noteworthy is the sudden rise at about 60% conversion. This is explained by cross-linking, which simultaneously diminishes the number of molecules and increases the average molecular weight. At about 75% conversion a new and sudden change is observed, the cause of which is not yet clear. Perhaps intramolecular interlinking, forming more compact molecules and leading to a lower viscosity in solution (the molecular weight was measured by this method), may be the explanation here.

Molecular ratio. Butadiene:Acrylonitrile

Conversion in %

Charging ratio A = 3.28   B = 2.09
C = 1.67   D = 1.25
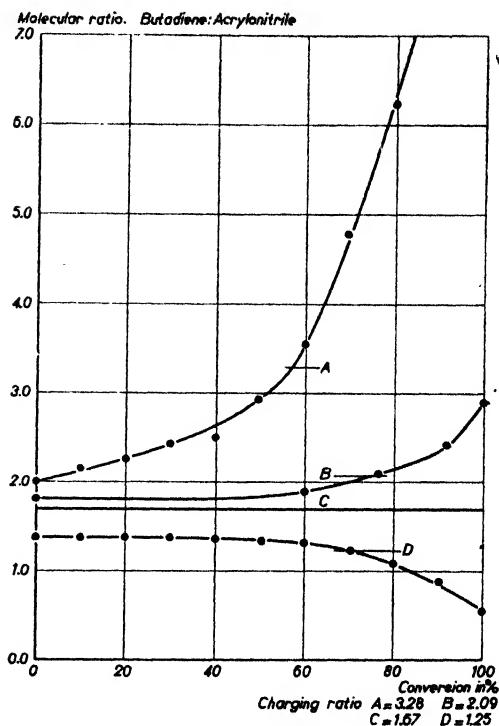
Fig. 16. Change of the ratio B/A in the polymerization of GRA.

Here a radical comes into being

Transfer of H
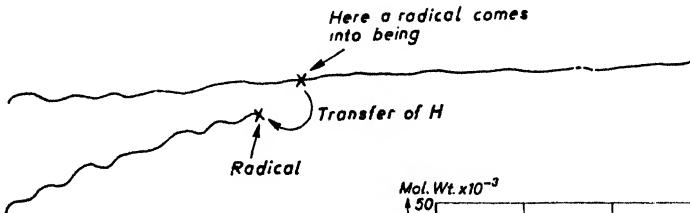
Radical

Fig. 17. Branching, due to a radical.

Mol. Wt. x10⁻³

Conversion
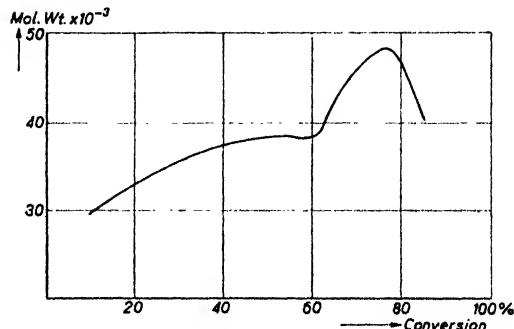
Fig. 18. Change of average molecular weight of G.R.S. during polymerization.

[1] F. T. WALL and L. F. BESTE, J. Am. Chem. Soc., 69 (1947) 1761.

Reviewing the picture, it will be obvious that the probability of irregular molecules being formed is greater than that of the formation of regular ones. This constitutes one of the main difficulties in attempting to synthesize regular molecules as they occur in nature. The fact that nature seems to build up its macromolecules in an essentially different way[1] may be responsible for the ideal regularity of the chains in natural rubber, cellulose and proteins. This leads to the very important conclusion that — except in some cases like nylon — mankind seems to be restricted to manufacturing its own sort of polymers, which differ from those in nature with respect to regularity: therefore with respect to crystallizing power and hence properties. There seem to exist two separate fields, one for men, the other for nature, unless scientific development will enable us to control polymerizations in a fundamentally better way. It is not our purpose to say that natural products are always superior for our uses, since in many cases lesser crystallizing power may be desirable.

§7. CHAIN AND GLOBULAR MOLECULES; NET BUILDING

In the third chapter we shall see that the physical properties of the polymers depend mainly on whether they possess linear or globular molecules. We owe to KIENLE[2] the knowledge as to how these two possibilities of formation can
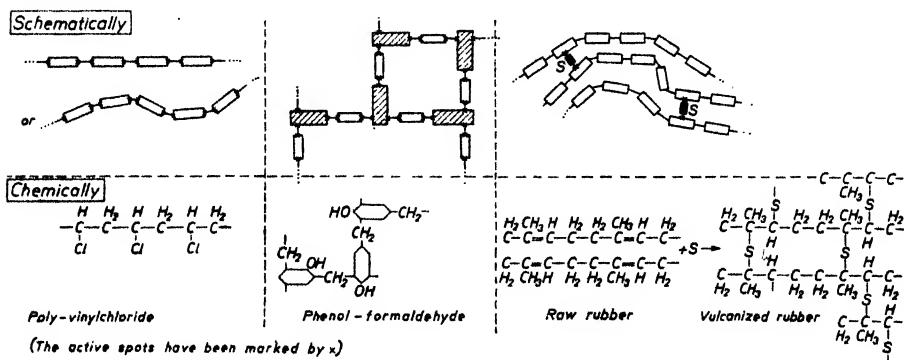
a. Chain formation due to a (2,2) - reaction (poly-styrene).

b. Formation of three - dimensional molecules by a (2,3) - reaction (phenol-formaldehyde resin).

c. Building of nets between chain-molecules by means of S-bridges (rubber-vulcanization).

Fig. 19. The three main principles of building macromolecules.

[1] There are reasons to assume that, for instance, natural rubber is not formed by polymerizing isoprene units but by condensing aldehydes, alcohols or similar compounds.
[2] R. H. KIENLE, Ind. Eng. Chem., 22 (1930) 590.

be determined beforehand. KIENLE classifies the monomer molecules according
· to whether they can react at two, three, or more spots, as (2)-, (3)-, or poly-
reactive. Thus, monostyrene is (2)- reactive, because after formation of a
radical (Fig. 3 p. 2) it can react in two directions, viz., to the left and to
the right. The glycerine molecule is indicated as (3)-reactive, because in the
process of esterification it has three active OH groups at its disposal. If it
reacts with a dicarboxylic acid we speak of a (3,2)-reaction.

The essential point now is, as shown in Fig. 19a, that *in (2,2)-reactions
chain-molecules can be formed exclusively*, whereas according to Fig. 19b,
in (2,3)-reactions three-dimensional structures can come into being.
The chain-molecules are also identified as thread, one-dimensional-, or linear
molecules, the globular ones as spherical or three-dimensional molecules.

An intermediate form between the two principal types is that in which
chain molecules are cross-linked later on by so-called bridges. A picture
arises as shown in Fig. 19c, which forms a certain transition from Fig. 19a
to Fig. 19b.

(a) Single molecule   (b) Wadding
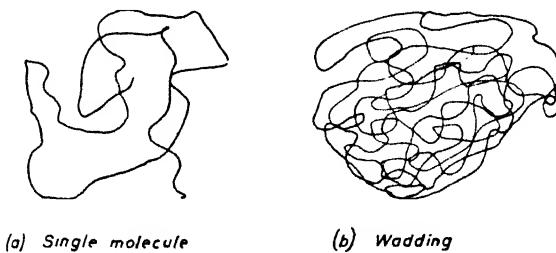
Fig. 20.   Coiled molecule and wadding structure.

We shall see in the fourth chapter, that the (2,2)-reactions lead mostly to
the formation of so-called thermoplastics, products which are hard in the
cold, but which soften easily when heated. On the other hand, the (2,3)-
reactions lead mostly to hard, infusible resinous products (e.g. "Bakelite")
and the interlinking often leads to materials with highly elastic rubber-like
properties.
  Later on, we shall revert again to the refinement of this picture, but at
present let it be mentioned that many of the extreme differences in properties
between materials containing chain molecules (Fig. 19a) and three dimensional
molecules (Fig. 19b) have been clarified by studying the effect of interlinking.

In connection with the above mentioned chain-forms of molecules it may

be said that in the last few years the expression *coiled molecules* has been used more and more. We owe the development of this picture especially to KUHN[1], as a result of which our insight has deepened considerably. In the beginning STAUDINGER considered the chain-molecules as rigid rods; today, however, they are looked upon rather as flexible threads which can form coils according to Fig. 20 . In this connection we sometimes also speak of a wadding structure[2].

§ 8.   THE PRINCIPAL MACROMOLECULES AND THEIR FORMATION[3]

The synthetic polymers can be classified in two groups according to the manner in which they are formed, viz., in derivatives of natural substances and in entirely synthetic materials.

a.   *Derivatives of natural substances.*

The natural substances which are used for the manufacturing of plastics are themselves, in most cases, already high-molecular, so that the process, in principle, comprises only the chemical modification of certain groups. The most important raw materials in question are compiled in Table 6 together with examples of derivatives manufactured from them.

From a chemical viewpoint the modification of such polymers is carried out in the same way as that of low-molecular substances; it is only the colloidal problems that usually cause difficulties. For instance, the macromolecules are—in consequence of their poorer solubility — less accessible to chemical reagents. In this connection we may point to the rayon industry, where just the dissolving of the cellulose constitutes one of the main difficulties (see chapter 11). Even when this has been surmounted, other possible disturbing reactions often have to be avoided, such as oxidations which may split the chains, or cyclizations which may interlink them. Apart from these — often very disturbing — secondary reactions, the effecting of many transformations hardly brings anything new and one can apply the classic methods of low-molecular chemistry: chlorination, acetylation, nitration, etc.

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[1] W. KUHN, *Kolloid - Z.,* **68** (1934) 1; **76** (1936) 258; **87** (1939) 3.
[2] R. HOUWINK, *Phys. Eigensch. und Feinbau von Natur- und Kunstharzen,* Leipzig 1934.
[3] For a general view: C. ELLIS, *The Chemistry of Synthetic Resins,* New York 1935; J. SCHEIBER, *Chemie und Technologie der künstlichen Harze,* Stuttgart 1943.

TABLE 6.
DERIVATIVES OF NATURAL POLYMERS

Natural polymer	Derivative
1. *Cellulose.* Structural unit	Cellulose triacetate
2. *Rubber.* Unit	Rubber hydrochloride
3. *Proteins.* Unit (R$_1$ and R$_2$ may be different)	Addition product with formaldehyde
4. *Drying oils.* In linseed oil: oleic acid . . $HOOC–(CH_2)_7–(CH=CH–CH_2)–(CH_2)_6–CH_3$ linolic acid . $HOOC–(CH_2)_7–(CH=CH–CH_2)_2–(CH_2)_3–CH_3$ linolenic acid $HOOC–(CH_2)_7–(CH=CH–CH_2)_3–CH_3$ In wood oil: $HOOC–(CH_2)_7–CH=CH–CH=CH–CH=CH–(CH_2)_3–CH_3$	Interlinking of linolic acid with alkylphenol resin.
5. *Natural resins.* Abietic acid	Addition product with maleic acid

b. Entirely synthetic materials.

Regarding the entirely synthetic materials we have already discussed polymerization and condensation reactions; the most important macromolecules which can be formed as a result are shown in Tables 7 and 8.

We wish to emphasize the fact that with regard to the polymerization-products which are derivatives of ethylene, the synthesis does not always start with ethylene; many of these products are in practice synthesized from acetylene. For a survey of the manufacturing methods we refer to p. 88.

It has appeared that, speaking very generally, the derivatives of natural substances and also the polymers based on ethylene are thermoplastic; those based on isobutene and on butadiene are rubbers and the condensation plastics are mostly thermosetting.

TABLE 7.

THE MOST IMPORTANT SYNTHETIC POLYMERS

1. *Based on Ethylene.*

$-[CH_2]_n-$ Polyethylene

$-(CF_2)_n-$ Polyethylene tetrafluoride

$$\left[\begin{array}{c} CH-CH_2 \\ | \\ | \quad | \end{array} \right]_x$$ Polystyrene

$$\left[\begin{array}{c} CH-CH_2 \\ | \\ Cl \end{array} \right]_x$$ Polyvinyl chloride

$$\left[\begin{array}{c} C-CH_2 \\ Cl_2 \end{array} \right]_x$$ Polyvinylidene chloride

$$\left[\begin{array}{c} CH-CH_2 \\ | \\ COOH \end{array} \right]_x$$ Polyacrylic acid

$$\left[\begin{array}{c} CH-CH_2 \\ | \\ OCO \\ | \\ CH_3 \end{array} \right]_x$$ Polyvinyl acetate

$$\left[\begin{array}{c} CH-CH_2 \\ | \\ C-OC_2H_5 \\ \| \\ O \end{array} \right]_x$$ Polyacrylic ethyl ester

TABLE 7. (CONTINUED)

$$--CH_2-CH-CH_2-CH--$$

Polyvinyl butyral

$$O \quad O$$
$$H \diagup$$
$$C$$
$$|$$
$$C_3H_7$$

Polyvinyl carbazole

$$\left[\begin{array}{c} CH-CH_2 \\ | \\ N \end{array} \right]_x$$

Polyallyl acetate and other esters

$$--\left[\begin{array}{c} CH-CH_2 \\ | \\ CH_2OOCCH_3 \end{array} \right]_x--$$

2. *Based on Isobutylene.*

Polyisobutylene (to be copolymerized with isoprene: GRI)

$$-\left[\begin{array}{c} CH_3 \\ | \\ C \quad CH_2 \\ | \\ CH_3 \end{array} \right]_x-$$

3. *Based on Butadiene.*

Polybutadiene (numbered Buna)

$$--\left[\begin{array}{cccc} H_2 & H & H & H_2 \\ | & | & | & | \\ -C-C & C-C- \end{array} \right]_x--$$

Polydimethylbutadiene (Methyl rubber)

$$--\left[\begin{array}{cccc} H_2 & CH_3 & CH_3 & H_2 \\ | & | & | & | \\ -C-C & = C - C \end{array} \right]_x--$$

Chloroprene or Neoprene (GRM)

$$--\left[\begin{array}{cccc} H_2 & Cl & H & H_2 \\ | & | & | & | \\ -C-C & C-C- \end{array} \right]_x--$$

Copolymer GRS (Buna S)

$$-\left[\begin{array}{cccccc} H_2 & H & H & H_2 & H_2 & H \\ | & | & | & | & | & | \\ -C-C & -C-C & -C-C \\ & & & & | & | \end{array} \right]_x-$$

Butadiene   Styrene

Copolymer GRA (Perbunan)

$$-\left[\begin{array}{cccccc} H_2 & H & H & H_2 & H_2 & H \\ | & | & | & | & | & | \\ -C-C & =C-C & -C-C- \\ & & & & & | \\ & & & & & CN \end{array} \right]_x-$$

Butadiene   Vinyl cyanide

TABLE 8.

THE MOST IMPORTANT CONDENSATION PRODUCTS

**1.** *Phenol-formaldehyde*
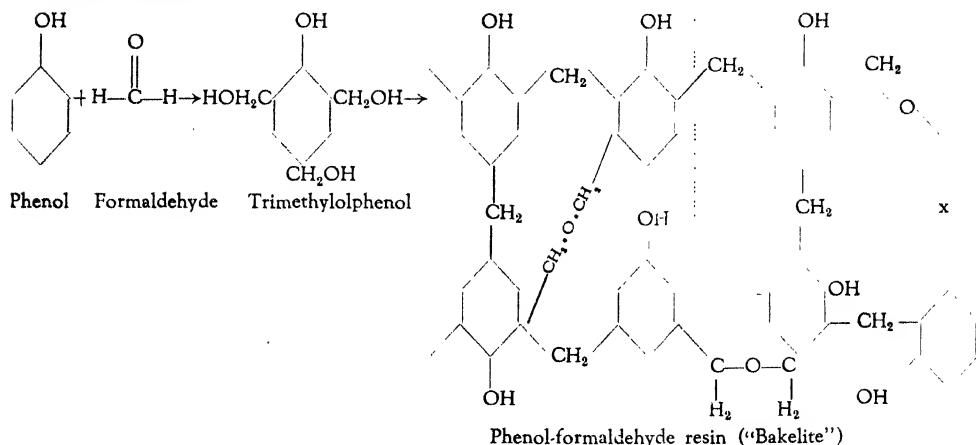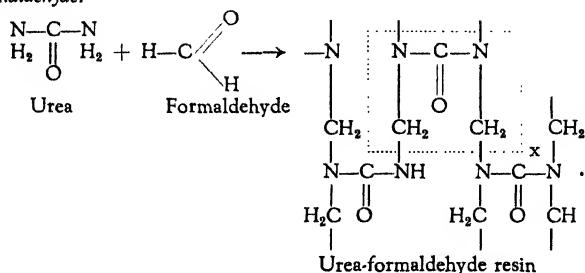
Phenol   Formaldehyde   Trimethylolphenol

Phenol-formaldehyde resin ("Bakelite")

2. *Urea-formaldehyde.*

Urea   Formaldehyde

Urea-formaldehyde resin

3. *Glycerine-phthalate.*

Glycerine   Phthalic acid

Glyptal resin

4. *Polyethylene tetrasulphide.*

$$CH_2\text{—}CH_2 + Na_2S_y \rightarrow \left[\text{—}CH_2\text{—}CH_2\text{—}\overset{\overset{S}{\|}}{S}\text{—}\overset{\overset{S}{\|}}{S}\text{—} \right]_x$$

CH₂—CH₂ + Na₂S_y → Sodium polysulphide

Cl   Cl
Dichloro-
ethylene

Polyethylene tetrasulphide
(Thiokol, Perduren)

5. *Superpolyamide.*

$$H_2N(CH_2)_pNH_2 + HOOC(CH_2)_qCOOH \rightarrow .. \qquad \text{—}[NHCO(CH_2)_qCONH(CH_2)_p]_x\text{—}$$

Diamine   Dicarboxylic acid   Synthetic polyamide (Nylon)

6. *Silicone.*

$$SiO_2 + MgRCl \longrightarrow \text{—}\left[\begin{matrix} R \\ \text{—}Si\text{—}O\text{—} \\ R \end{matrix} \right]_x\text{—}$$
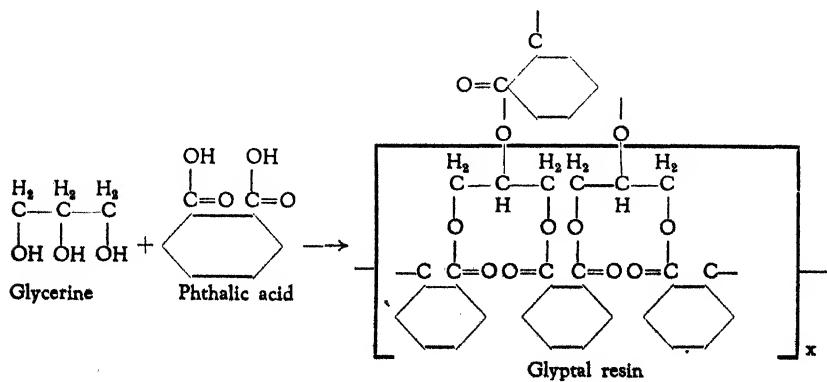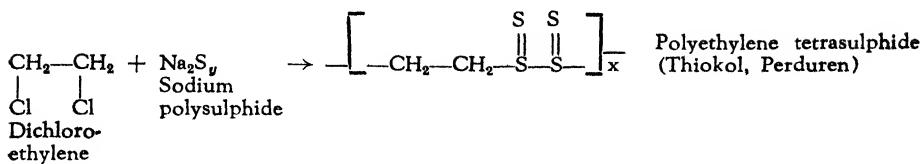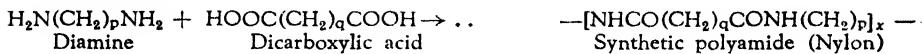
Silicones
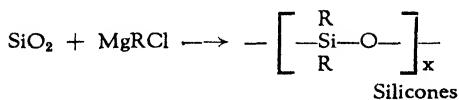
CHAPTER II

BONDS INSIDE AND OUTSIDE THE MOLECULES [1]

§ 9. BINDING ENERGY

The energy content of the bonds between two atoms in a molecule is very high. When, on the other hand, the atoms of two neighbouring molecules are only in contact with one another, their cohesion (a measure of the binding-energy) is often very small. Consequently, a significant increase of the binding energy must take place when two monomer units polymerize. Therefore, much more energy is required to break up the units of a polymer than to separate two neighbouring molecules in the monomer.

The bonds within the molecule, rich in energy, are called the *primary bonds*, those *between* the molecules, poorer in energy, the *secondary bonds*. One also speaks sometimes of principal and secondary valences. As is seen from Table 9, the energy-content of the primary bonds amounts to about 100 to 200 kcal per mole and for the secondary bonds from 1 to 10 kcal per mole.

In the bonds with the higher energy-content the interatomic distance [2] is smaller (1 — 1.5 Å) than in those with the lower energy-content (3 — 4 Å).

TABLE 9.
ENERGY-CONTENT BETWEEN PRIMARY AND SECONDARY BONDS IN MOLECULES [3]

Primary Bonds			Secondary Bonds		
Bond	Distance in Å	Energy content in kcal/mole	Group	Distance between adjacent molecules in Å	Cohesion in kcal/mole
C-H	—	92	—CH₃	3—4	1.78
C-C (aliphatic)	1.55	71	=CH₂	3—4	0.99
C-C (aromatic)	1.45	96	—OH	3—4	7.25
C=C	1.20	125	—CO	3—4	4.27
C=O	1.10	203			

[1] For a summary see H. MARK, *Physical Chemistry of High Polymeric Systems*, New York 1940; O. K. RICE, *Electronic Structure and Chemical Binding*, New York 1940.

[2] 1 Å (1 Angstrom Unit) = 10^{-8} cm.

[3] R. HOUWINK, *Elastomers and Plastomers*, Amsterdam 1949, Part I, Chap. by VAN AMERONGEN.

This can be understood by consideration of the potential curves between two atoms [1]. The potential troughs are deeper and are closer together for the primary bonds. As a very rough approximation one might say: the closer the atoms approach each other, the more energy is required to separate them again. As is seen from Table 10, the distance between the atoms, after the polymerization has taken place, finds expression in the density.

TABLE 10.

CHANGES OF DENSITY BY POLYMERIZATION

Substance	Density	
	Monomer	Polymer
Styrene	0.903	1.05
Isoprene	0.679	0.957
Isobutylene	0.62	0.93

In order to illustrate further the present conceptions regarding the molecular structure, we show in Fig. 21 models of dodecane as an example of a short chain molecule and of benzene as an example of a closed ring.


a. Dodecane

b. Benzene
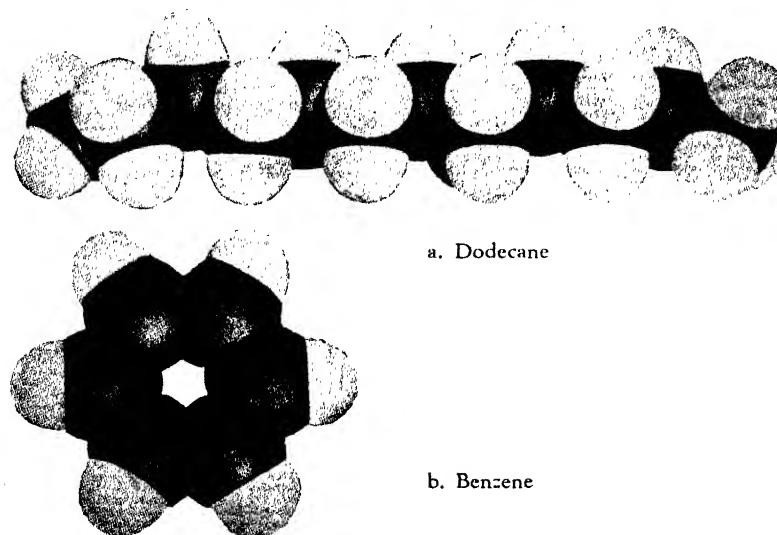
Fig. 21.   Molecular models.

Both primary and secondary bonds may be subdivided into groups, and it is possible to indicate approximately the manner in which the binding

[1] R. HOUWINK, *Elasticity, Plasticity, and Structure of Matter*, Cambridge 1937, p. 25.

forces decrease with distance from the atom centres. Obviously this is of great importance with regard to the mechanical properties of the substance. Long range forces will allow larger deformations than short range forces; the latter give rise to brittleness.

§ 10. P R I M A R Y   B O N D S

a. Heteropolar or ionic bonds.

Positive and negative ions (Na^+ and Cl^-) attract each other by electrostatic forces, which under favourable circumstances may lead to a bond. The attracting force decreases with $1/r^2$ providing an example of long range forces.

b. Homopolar or atomic bonds.

Two neutral atoms A and B can attract each other, the so-called valency electrons forming a pair and belonging jointly to both nuclei (H_2, Cl_2). To this end it is often necessary that the atoms be brought into an activated state. The C-C bond and the C-H bond in organic chemistry are examples. When two similar atoms are united by means of an atomic bond to form one molecule, a nonpolar molecule is obtained (H_2); when the atoms are different, then, in general, the molecule is polar (Ag I in the gas state).

c. Metallic bond.

This is left out of consideration here.

§ 11. S E C O N D A R Y   B O N D S

a. Dipoles and multipoles.

Ions or molecules in which the centres of gravity of $+$ and $-$ charges



a. parallel   b. non-parallel
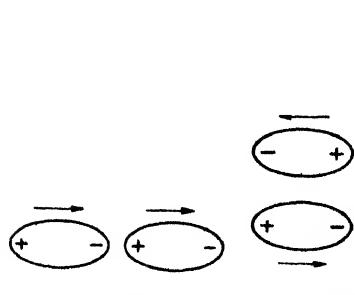
Fig. 22. Two different possibilities in the mutual attraction of dipoles.

Fig. 23. Dipole-dipole attraction of diethyl ketone and water (parallel-adjustment).

do not coincide form so-called permanent dipoles; OH ions and HCl molecules are examples thereof. The mutual attraction can take place in two ways, as shown in Fig. 22a and 22b.

In both cases the attractive power decreases with $1/r^3$; in the non-parallel position the force is twice as large as in the parallel position. The so-called association in liquids is often based on dipole-attraction and in Fig. 23 it is shown how a water molecule is attracted by diethyl ketone because of this action.

Besides the fixed dipoles, the *induced dipoles* are known. The explanation of their formation is that by external influences (an electric field or under influence of ions or other dipoles), the centre of gravity of the negative charge relative to the positive nucleus of a neutral atom is shifted. The dipole moment then is equal to a × d, where a = shifted charge and d = the distance between the centres of gravity of the nucleus and the electron charge. Here, the binding force decreases much quicker than in the case of permanent dipoles, viz., by $1/r^7$. In general we designate the substances in which induced dipoles can form, as *polarizable*.

b. *Dispersion forces.*

The frequent movements of the electrons in the atoms bring about continually changing dipoles which continually induce new, changing dipoles in the neighbouring atoms; this leads to the so-called *exchange- or dispersion forces*. The attractive power which is formed as a result decreases by $1/r^6$ and consequently is not far reaching. The dispersion forces exist universally, so that — properly speaking — one has to reckon with them in all cohesion phenomena. Sometimes they are designated VAN DER WAALS's forces, although one sometimes finds all secondary forces considered under this name (see later).

c. *Interaction of the various forces.*

Naturally, there exists the possibility of interaction between these various kinds of forces, which leads to the so-called VAN DER WAALS's attraction.

In order to give an indication of the proportions involved, we refer to the examples of Table 11. .

In Fig. 23, showing the attraction of water to diethyl ketone, at least two kinds of bonds are interacting: the dipole-dipole attraction and the dispersion forces. Moreover, we may presume that the water molecule will excite induced dipoles, e.g., in the CH_3-groups situated nearby, which will furnish an additional interaction contribution.

TABLE 11.

RATIOS OF SOME ATTRACTIVE ENERGIES

Molecule	Dipole energy / Dispersion energy	Induction energy / Dispersion energy
H_2O	1.53	0.20
HCl	0.29	0.05
NH_3	1.02	0.11

The importance of the strength of the secondary bonds for polymers will be discussed on page 43. It will appear that when there is no special crystallizing capacity the following classification can be made:

> rubbers have a cohesion of 1—2 k cal/mole
> plastics ,, ,, ,, ,, 2—5 ,, ,,
> fibres ,, ,, ,, ,, >5 ,, ,,

§ 12. MOLECULAR SIZE AND BINDING ENERGY

The longer the molecule, the greater will be the mutual secondary binding energy. This is apparent from low molecular chemistry in which we find (Table 11a) an increasing molar cohesion in ascending the paraffin series.

TABLE 11 a

MOLAR COHESION IN THE PARAFFIN SERIES

Molar cohesion in cal	2160	3570	4510	5595
Paraffin	CH_4	C_2H_6	C_3H_8	C_4H_{16}

When developing this concept further it is imaginable that above a certain molecular weight the total secondary energy exceeds the primary energy, which according to Fig. 24 is confirmed as regards polyoxymethylene. At a degree of polymerization of about 140, the melting point exceeds the decomposition temperature, which means that the primary bonds are already disrupted at a temperature at which the secondary bonds still possess sufficient strength to maintain the solid state. The conclusion is that on increasing the molecular weight these substances can only exist in the solid state. To make them flow it is then necessary to apply external pressure, a practice which is generally followed in the moulding of polymers. Here lies the root of the fundamental difference between casting of metals and moulding (under pressure) of polymers. In metals there are no chain molecules of an organic nature in which the energy content of the primary bonds can be surpassed

by the sum of the secondary energies all along the chain. There is only one
type of bond in metals (and in inorganic crystals in general), and these are
all disrupted at about the same temperature. This means that there is a sharp
melting point (see Fig. 48 on the transformation interval).
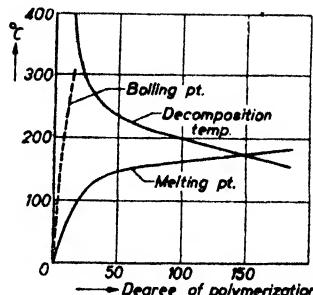
Fig. 24. Change of the physical
constants of polyoxymethylene
with increasing molecular
weight.

The phenomenon of increasing cohesive energy as a consequence of an
increase in the molecular weight in relation to the mechanical properties will
be further discussed on page 35.

§ 13. MOLECULES AND MICELLES

In the literature one often comes across the concept of micelles and
therefore we wish to say a few words about it. Certain authors speak of micelles
when certain molecules because of secondary forces, cling together as an
aggregate of colloidal[1] size, while others designate the molecules themselves
as micelles when they have reached colloidal dimensions.

a	b	c
Amorphous	Crystalline	Oriented crystallites
	micelles	
	(crystallites)	
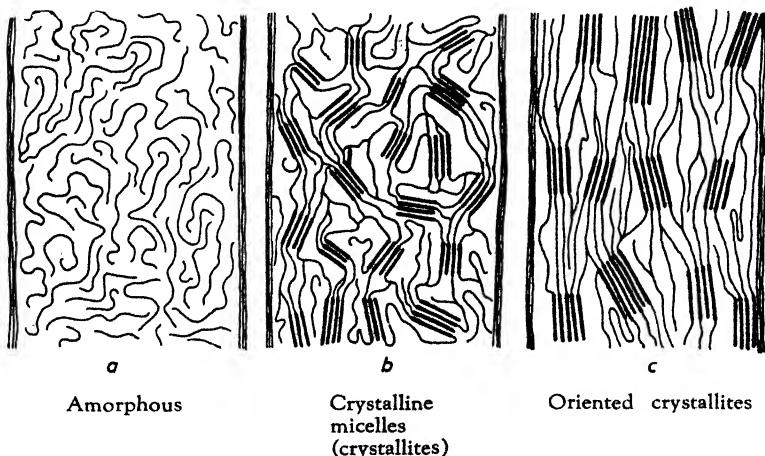
Fig. 25. Amorphous and crystalline polymers[2].

[1] The limits of the colloidal dimensions are 10 Å and 10⁴ Å (10^{-8} cm and 10^{-4} cm).
[2] From T. ALFREY, *Mechanical Behavior of High Polymers*, New York 1948.

We shall use the former concept. The micelles can be divided into two groups, according to whether or not they possess crystalline parts. Such crystalline portions, generally designated as crystallites, are shown in Fig. 25b. Here the protruding fringes connect the crystallites with one another. In Fig. 25c these crystallites are oriented, a point which we shall discuss on page 46. In connection with cellulose (see page 193) and rubber we shall come across familiar examples of such crystallites.

It is interesting to note that the dimensions of the crystallites in high polymers may be of the same order of magnitude as those in a material like asbestos. This is shown in Table 12.

TABLE 12.

AVERAGE WIDTHS OF CRYSTALLINE AREAS [1]

	Width in A°
Fibrous asbestos	200
Highly stretched rubber	80
Drawn polyamide fibre	200
Highly orientated viscose rayon	50—200

It will be shown that the formation of crystallites and, in general, micelles, is influenced by many external factors. For instance, an increase of concentration in a solution can bring the molecules nearer to each other, thus creating the possibility of a better secondary cohesion, i.e., of micelle formation. Moreover, an orientation may give the opportunity to the random molecules to arrange themselves in such a way as to enter into a crystalline lattice (page 36).

The formation of crystallites is easier when the molecules are longer, since they are less mobile. This is borne out by the fact that in a solution the concentration at which micelles are formed is lower for longer molecules[2].

Substance	Conc. (in %), at which micelles are observed (20° C)
Na caproate	10
Na laurate	0.8
Na oleate	0.003

1. FANKUCHEN and H. MARK, *J. Appl. Phys.*, 15 (1944) 364.
2 K. HESS, *Fette und Seifen*, 49 (1942) 81.

CHAPTER III

PHYSICS AND COLLOID CHEMISTRY OF POLYMERS [1]

It is particularly convenient to investigate the connection between structure and properties in polymers. We are able to change practically at will the molecular size and the resultant changes in properties can be followed easily either in solution or in the solid state.

§ 14. MECHANICAL BEHAVIOUR

a. The mechanical properties and their definitions [2].

In order to investigate the mechanical properties of solid substances it is best first to study the tension-elongation diagrams, as shown in Fig. 26 for
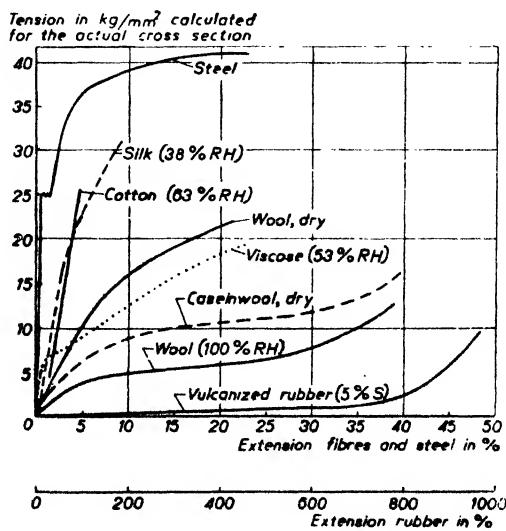
Fig. 26. Stress-strain curves for various materials.

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[1] Many of the problems of this chapter are extensively treated by KURT H. MEYER, *Natura and Synthetic High Polymers*, New York 1942.
[2] G. T. ALFREY, *Mechanical Behavior of High Polymers*, New York 1947.

31

different materials. For steel, HOOKE's law is valid up to 25 kg/mm², i.e., tension and elongation are proportional to one another:

$$\triangle L = \frac{\sigma}{E} \quad \ldots \ldots \ldots \ldots \ldots \ldots (3)$$

where $\triangle L$ = elongation, σ = tension, E = modulus of elasticity.

This cannot be said of all substances and therefore one cannot always refer to a *modulus of elasticity*; compare, e.g., the curve for casein wool.

Below a load of 25 kg/mm², where the flow-limit (so-called *yield value*) is, steel behaves as purely elastic; when exceeding this limit, it starts flowing until breaking occurs.

For constructions the yield value is at least as important as the tensile strength, because in constructions no flow is admissible. For the majority of plastics, the yield value does not reveal itself as sharply as in metals, because often from the very beginning the elongation is accompanied by plastic deformation. Then this is not a purely elastic deformation.

The *elastic part of the elongation* is a particularly important property, which determines whether or not a deformation is *high-elastic*. The following definitions have been proposed [1]:

A deformation is called *low-elastic*, when a test piece of length *l* stretched to *nl*, recovers over a distance smaller than $\frac{l}{100}$.

A deformation is called *high-elastic*, when a test piece of length *l* stretched to *nl*, recovers over a distance larger than $\frac{l}{100}$.

A deformation is called *rubber-like high-elastic*, when a test piece of length *l* stretched to *nl*, recovers over a distance larger then *l*.
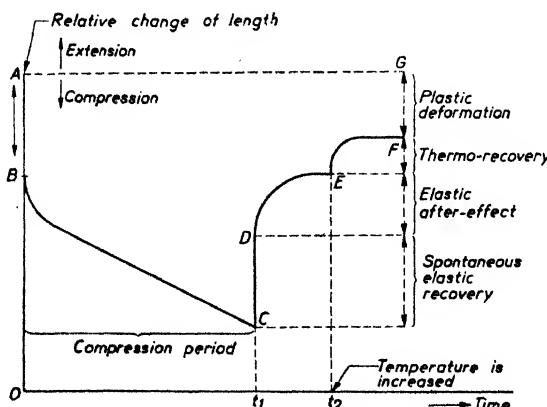

Fig. 27. Some possibilities of recovery for a polymer after having been compressed.

[1] R. HOUWINK, *Elasticity, Plasticity, and Structure of Matter*, Cambridge 1937, Chap. I.

It is necessary to return to the differentiation between elastomers and plastomers, expressions frequently encountered in literature. Under *elastics* we will classify the rubbery elastic materials; the term *plastics* will be restricted to those substances which on deformation show an elastic recovery less than 100% of the original length.

Many recoveries of polymers are not *spontaneously elastic*. In Fig. 27 it is shown, how after a compression during the time t_1 a spontaneous recovery, CD, first takes place which, however, gradually ceases (DE). Only after an increase of temperature (at t_2) is the final state reached; FG appears to be the permanent plastic part of the deformation. DE is sometimes called the *elastic after-effect* and EF the *thermo-recovery*. Both are retardation effects which are brought about because large molecules are hampered in their movements.

Fig. 28 gives a more detailed picture [1] of combined elastic and plastic effects as they are often encountered in polymers.


Fig. 28. Deformation and flow under constant load plotted against time for polyisobutylene fractions of different molecular weight.
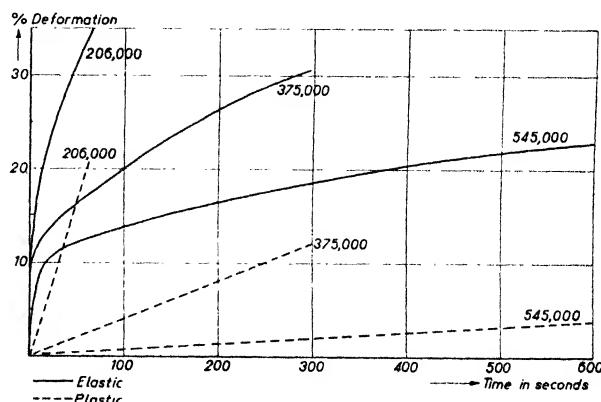
The elastic part of the deformation for each fraction is obtained by subtracting the dotted curve (plastic part) from the curve drawn in full (total deformation). The fact that the dotted and the full curves for a certain fraction run practically parallel proves that the elastic part remains constant during the deformation process. It is according to expectation that the lower polymerized fractions are more easily deformable and that the deformation is relatively less elastic.

It should be pointed out that the *elastic part* of the deformability is often most important for judging quality. For example the thermoplast polyisobutylene which shows an extension at the breaking point of 1000%, recovering, however,

[1] R. L. ZAPP and F. P. BALDWIN. *Ind. Eng. Chem.*, 38 (1946) 948.

only $10^0/_0$ of this extension, is designated as inferior, from the standpoint of the rubber technician, since vulcanized natural rubber with an extension at break of only 600% is 90% elastic.

Moreover, the *high elasticity temperature*, i.e., the temperature at which a substance becomes high-elastic, is of great importance because, in practice, only such materials of which rubbery high-elasticity temperatures lie in the region of room temperature, are useful rubbers.

b.   Tensile strength.

One might expect to be able to calculate the tensile strength from the energy content of the bonds between the atoms, and such calculations actually exist. However, it appears that the tensile strength found experimentally is 500 to 1000 times smaller than the calculated one, as is seen from the data of Table 13. [1]

TABLE 13.

DISCREPANCY BETWEEN OBSERVED AND CALCULATED
TENSILE STRENGTH

	Tensile strength in kg/mm^2.	
	Observed	Calculated
Glass	3.5—8.5	1100
Phenol-formaldehyde resin (C-state)	7.8	4300
NaCl crystal	0.6	300

We shall see on p. 148 that this is attributed to faults in the solid substance which cause a notch-effect. In the chain polymers the long molecules are themselves very strong on account of the primary bonds.

1. Orientation

It can easily be understood with the aid of Fig. 29 that linear polymers with sufficient molecular length have a greater strength than, for example, asphalt.

The cohesion surface of the chain molecules, which for simplicity's sake are here supposed to have parallel orientation, is larger than that of the globular particles. As a first approximation [2] the following formula seems to hold:

$$\sigma = K\, n\, \alpha \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ (4)$$

[1]   R. HOUWINK, *Trans. Faraday Soc.*, 32 (1936) 122; J. H. DE BOER, *ibid.*, 32 (1936) 10.
[2]   See for further explanation: P. J. FLORY, *J. Am. Chem. Soc.*, 67 (1945) 2048.

where σ = tensile strength, K = constant, n = number of chain elements, a = mole cohesion per monomer group.


a) Chain molecules
(oriented)

b) Globular particles
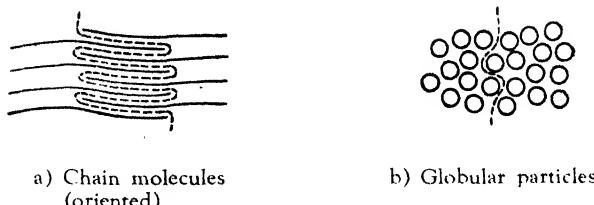
Fig. 29. The longer the particles the greater the (dotted)
cohesion surface.

A minimum polymerization degree between 40 to 80 appears to be necessary to obtain a reasonable mechanical strength. A high strength is reached sooner when the orientation, or better still when the crystallization, is favoured in spinning or similar operations. A comparatively small amount (10—15%) of low molecular (polymerization degree < 150) constituents has a detrimental influence on the mechanical strength: they act as lubricants.

In practice the orientation is never as complete as is represented in Fig. 29a and for that reason (among others) the proportionality according to (4) is not confirmed experimentally. However, an increase of strength with increasing chain length is clearly detectable, (Fig. 30a). That there is a tendency toward a maximum may be due to the fact that above a certain chain length the cohesion becomes greater than the strength of the molecule itself, so that the chain breaks while stretching.
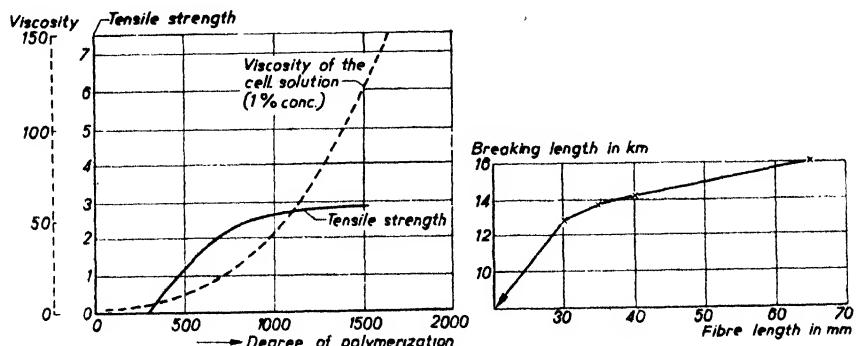
a. The strength of cellulose increases with increasing *molecular* length.

b. The strength of a thread increases with increasing *fibre* length. [1]

Fig. 30. In the microscopic as well as in the macroscopic domain the strength of substances built up with oblong particles increases with the length of these particles.

[1] A. ZART, Chemie, 55 (1942) 11.

For comparison, it is seen in Fig. 30b that the strength of a spun yarn increases with the length of the fibres used for spinning. It is thus inferred that in the macroscopic domain similar occurrences take place as in the microscopic domain.

2. Crystallization.

Apart from the degree of orientation, another very important problem is the crystallization of the material on stretching.

Crystallization means that the chains fit into a lattice so that the mutual attracting groups have the opportunity of snapping into each others potential troughs. Experiments have shown that for materials with chain-molecules no reasonable strength is observed unless this condition is fulfilled. It will be shown on p. 47 that this ability is decisive in characterizing the substance as a plastic, a fibre or a rubber. On p. 13-16 it has already been discussed how this crystallizing capacity is correlated with the regularity of the chains.

3. Interlinking.

According to KIENLE (p. 16) the situation for both groups of substances, as represented in Fig. 29, changes immediately when active spots on the surface of the particles come into play. In the chain molecules this leads to the formation of nets (see Fig. 19, p. 16), part of the secondary forces being replaced by primary ones. A well-known example, already referred to, is the vulcanization of rubber. By heating with sulphur, bridges are formed between the rubber chains, and the improvement in strength[1] and in capacity
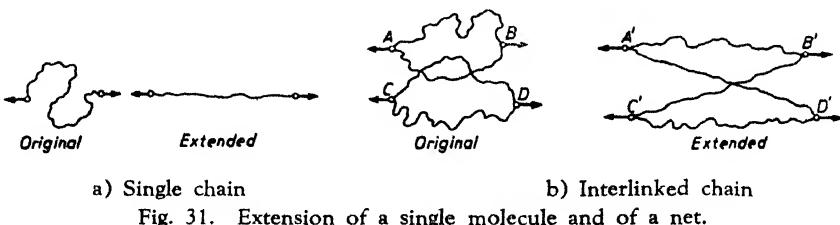
a) Single chain   b) Interlinked chain
Fig. 31.   Extension of a single molecule and of a net.

for elastic recovery which can thus be obtained is explained as shown in Fig. 31. Each single chain if stretched out adheres to its neighbour only by secondary forces and therefore slips off easily. The chains interlinked in A, B, C and D, on the contrary, have acquired adhesion spots of great energy

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[1] Actually the explanation of the increase of strength by interlinking is more complicated than presented here.

content, which on the one hand avoids slipping-off and on the other hand renders the recovery possible. For raw rubbers for instance, the strength increases by vulcanization from 10 to about 150 kg/cm². Also the heat resistance increases, as the interlinked spots are not loosened when increasing the temperature. FLORY [1] has shown that the loose ends of the chains interlinked in a network still have an important influence on the mechanical properties of the final product. Regarding substances with globular molecules, the best studied example, in which the formation of bridges improves the above named properties, is the phenol-formaldehyde resin of Fig. 102 (page 148). Here the CH_2 groups form the bridges which couple the benzene nuclei; in Chapter 6 we shall again return to this subject.

The hardness measurement gives an impressive confirmation of these general reflections, and in this connection we refer to Table 14. The hardness of some linear polymers measured by two different methods has been compared [2] with that of some interlinked polymers. As was expected, the hardness

TABLE 14.

COMPARISON OF THE HARDNESS OF LINEAR AND
INTERLINKED POLYMERS

Substance	Hardness (impression by a ball)	Scratch hardness
Linear polymers.		
Polystyrene	18	1.6
Rubber (unvulc.)	1—3	—
Acetylcellulose	6—8	1.6
Silk protein	3—5	—
Interlinked polymers.		
Phenol-formaldehyde resin	38—55	2.9
Urea-formaldehyde resin	35—50	2.9
Glyptal	30—35	2.8
Rubber (vulc.)	35—50	2.7

of the latter is much greater, because the chains cohering only by secondary bonds are more easily separated from each other than the chains of the interlinked polymers (cohering by primary bonds). Of particular interest is the comparison of un-vulcanized rubber with vulcanized, because here the effect of the sulphur bridges reveals itself as imparting 30 times greater resistance against impression in the ball test.

While discussing the secondary bonds it was shown that there are various

[1] P. J. FLORY, *Chem. Revs*, 35 (1944) 51.
[2] According to : H. MARK, *Trabajos del IX Congreso Internacional de Quimica Pura y Aplicada*, IV (Madrid 1934).

types. One may naturally expect that the properties of a substance will depend largely on the nature of the secondary bonds. We should point out here certain experiments in which, for a certain molecule, the side groups were systematically modified, and the properties of the products thus obtained were studied. We refer to a study [1] in which cellulose esters were furnished with side groups of increasing length [2]. Fig. 162 (p. 211) shows that the strength thereby decreases continuously and that the elongation at break — for the greater part a permanent set — increases. Supposing that the side-chains stand perpendicularly to the cellulose chains, then their increasing length signifies that the cellulose molecules are further and further removed from each other, which may explain the decreasing cohesion.

In spite of the great importance of the tensile strength as a measure in the testing of materials, the so-called *flexural* strength, which is further discussed on page 75, has unfortunately become more popular.

This is to be regretted, since determining the tensile strength automatically involves the determination of the stress-strain diagram as a whole, giving useful information on the modulus of elasticity, the yield value and the elongation at break.

c. The impact strength or impact resistance

This measures the amount of energy necessary to cause breaking, and theoretically this should be expressed by the hatched area in Figure 32. (Energy $= l \times \sigma$; one can say that the degree of brittleness is measured in this way.)
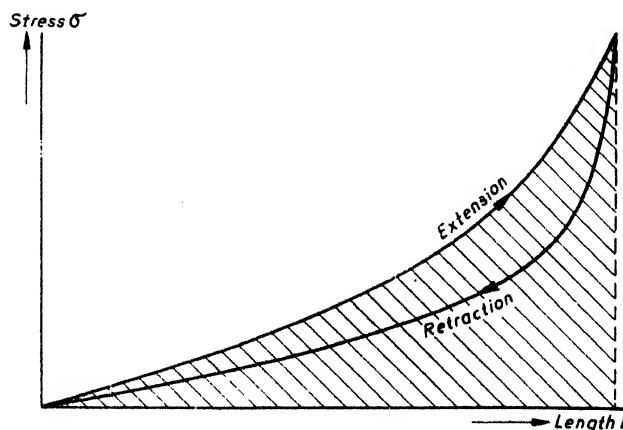

Fig. 32. Energy at break and hysteresis.

[1] M. HAGEDORN and P. MOELLER, *Cellulosechemie*, 12 (1931) 29.
[2] See p. 118 for similar investigations on polyvinyl derivatives.

In practice the situation is much more complicated as appears[1] when the values found for this surface are compared with data recorded on impact resistance testing apparatus, in which a bar is broken by a falling pendulum, the energy absorbed being measured (Table 15). The ratio $\dfrac{\text{theoretical value}}{\text{practical value}}$ appears to vary between 0.7 and 4.8.

TABLE 15.

THEORETICAL AND PRACTICAL VALUES FOR THE IMPACT RESISTANCE
(ft. lb)

Material	Theoretical (area according to Fig. 32)	Practical (Izod test, see Fig. 55, p. 76)	Ratio: $\dfrac{\text{theoretical}}{\text{practical}}$
Phenol-formald. , woodflour filled	0.63	0.13	4.8
,, , fabric ,,	1.68	2.30	0.7
,, , mineral ,,	0.10	0.15	0.7
,, , no filler	0.95	0.24	4.0
Polystyrene	0.45	0.18	2.5
Acrylic resin	0.69	0.22	3.1

Another complication is that with plain test-bars other results are obtained than with notched bars. In practice this means that objects with irregular surfaces or possessing incisions behave differently compared with plain and undamaged objects. It will be clear that the most decisive test in such cases is that with notched bars (p. 76). Therefore this type of tests has acquired rapidly growing importance.

It will appear (p. 158) that the impact resistance depends to a great extent on the kind of filler. Generally speaking, coarse fillers increase the impact strength of rigid materials, which is ascribed to their damping effect on mechanical shock waves, transforming the latter into heat[2]. This effect appears[3] from Table 16, where the rate at which free torsional oscillations of test cylinders disappear (expressed by the damping capacity) is compared with the impact resistance for four mixtures of phenol-formaldehyde resin with fillers of increasing coarseness.

d. Hysteresis.

The *hysteresis*, expressing the amount of energy which is lost during a cycle of extension and retraction, is measured by the area between these two curves in Fig. 32. This property is important for motor car tyres because it is responsible for the so-called heat-build-up during driving.

[1] TH. HAZEN, *Modern Plastics*, 21 (1943) 103, 144.
[2] N. A. DE BRUYNE and J. N. MAAS, *Aircraft Eng.*, 8 (1936) 289.
[3] H. LEADERMAN, *J. Applied Mechanics*, 6 (1939) A 79.

TABLE 16.

DAMPING CAPACITY AND IMPACT RESISTANCE IN RELATION WITH
TYPE OF FILLER

Type of filler	Damping capacity in %	Impact resistance (Izod) ft lb/in of notch
None	8.9	0.25
Wood flour	31.1	0.3
Fabric	33.2	2.4
Cord	36.6	7.0

e. Fatigue.

A final test to evaluate the strength of a material is the *fatique test*, in which a stress is applied repeatedly with high frequency. The number of cycles, necessary for break, is considered to be a measure of the fatigue resistance. All the mechanical tests, described under *a — e* together furnish a comprehensive idea of the technical usefulness of a high polymer, to which for special applications (lacquers, foils, fibres, artificial leather) special tests are added. Regarding the execution of such tests we refer to Chapter 4.

f. High elasticity.

We recall to mind that the crystallization of a melt is due to the fact that at a certain temperature (solidification temperature) the "Brownian motion" of the units ceases, so that they arrange and fix themselves in a crystalline lattice. The more complicated and bulky the units are built — for simplicity's sake let us speak of molecules — the more difficult it will prove to make the molecules fit exactly into the lattice [1]. This may be the reason why it is not easy to bring to crystallization a substance like abietic acid (see formula page 19), which constitutes the principal element in colophony; an amorphous substance is formed more easily the more asymmetrical are the molecules. This does not mean that all *atom-groups* in the abietic acid come to a complete standstill when frozen in. It is very well possible that the molecules as a whole cannot move any more — e.g., because the COOH groups, which here have the strongest dipole-moment, are completely fixed — whereas other atom-groups still vibrate and swing to and fro. Under these circumstances we can say, in accordance with KUHN's proposal, that the *macro-Brownian motion* (abbreviated to macro-B.M.) of the entire abietic acid molecule is fixed but that the *micro*-B.M. of the single groups is still free. [2]

[1] Referred to p. 48 for a full discussion of these phenomena in relation to the transformation interval.
[2] W. KUHN, *Angew. Chem.*, **51** (1938) 640.

For the appearance of ideal [1] rubber-like high elasticity, KUHN put forward the following two conditions:

1. The micro-B.M. of the molecules should be entirely free.
2. The macro-B.M. of the entire molecule should be prevented.

In order to understand these fundamental conditions we point in the first place to the experimental fact that, for natural rubber, in the elongation range of 0 to about 400% the tension of a stretched specimen increases proportionally to the absolute temperature:

$$\sigma = C T \dots \dots \dots \dots \dots \dots \dots \dots (5)$$

in which C = constant.

A calculation [2], starting from this fact leads to the very important conclusion that an elongation or a contraction within this range (0 to 400%) takes place *without change of internal energy*:

$$\left(\frac{dU}{dl}\right)_T = O, \dots \dots \dots \dots \dots \dots \dots (6)$$

where U is the internal energy.

The same is found in ideal gases, where the change in internal energy on expansion is also equal to zero. In ideal gases this is obvious, because the molecules exert no influence on each other and so there is no reason for any change in internal energy on expansion. In rubber, however, it seems difficult to suppose that the molecules should have no influence whatsoever on each other. A more reasonable explanation seems therefore to be that the molecules do influence each other to a certain extent, but that in the region between O and 400% positive and negative influences neutralize each other [3].

It can be shown [4] from the second law of thermodynamics that when $\left(\frac{du}{dl}\right)_T = O$, all work which is performed is equal to the change in entropy, which may be written:

$$\left(\frac{dA}{dl}\right)_T = - T \left(\frac{dS}{dl}\right)_T \dots \dots \dots \dots \dots (7)$$

where A = work, S = entropy.

---

[1] By ideal high elasticity we understand that particular elasticity for which equation 5 holds. In practice the conditions for this are not usually fulfilled exactly, and then KUHN's conditions undergo a restriction inasmuch as the micro- and the macro-B.M. are not entirely free and not entirely restricted, respectively.

[2] K. H. MEYER and C. FERRI, *Helv. Chim. Acta*, 18 (1934) 570. A summary is given by K. H. MEYER, *Natural and Synthetic High Polymers*, New York 1942; E. GUTH, H. M. JAMES and H. MARK, *Advances of Colloid Science*, New York 1946, p. 253.

[3] See page 40, footnote 1.

[4] R. HOUWINK, *Z. phys. Chem.* A 183 (1938) 209. The positive effects are ascribed to the deformation of valence angles in the chains, the negative effects to crystallization phenomena.

How shall eq. (7) be interpreted from a molecular point of view? One may say that nature strives toward a maximum of entropy, that means toward as great a disorder of the molecules as possible. Eq. (7) shows however that the work done on the rubber results in a decrease of entropy, that is, in a better ordering of the molecules (orientation). The molecules will thus counteract this by trying to get back to their maximum randomness, which will be felt as a force of contraction. It has also been put in the following way. The oriented molecules obey the law that entropy strives toward a maximum by hammering each other in such a way that the original disordered state tries to restore itself. The strongest hammering therefore takes place perpendicularly to the orientation direction and it increases as the temperature rises.

It is the power to become elongated without change of the internal energy which has led to KUHN's first condition for ideal rubber-like high elasticity, because if the micro-B.M. of the atom groups should not be free, this would mean that the molecules would hold on tightly to one another over their whole length. Under these conditions, however, an elongation would also bring about a change in the internal energy [1].

The second condition of KUHN is necessary because in the case of free macro-B.M. the chain molecules, while elongating, would flow away, thus destroying the disorder brought about artificially; the entropy-difference would disappear and consequently the cause of the recovery.

In the liberty of the micro-B.M. and the prohibition of the macro-B.M. lies perhaps the briefest description of the requirements for the appearance of ideal high elasticity.

On this basis it is easily understood why the existence of rubber-like elasticity is limited to a certain temperature range. At lower temperatures the micro-B.M. stops; the substance becomes stiff. Too high temperatures set the macro-B.M. free and the substance starts flowing. Here, the favourable action of bridges as formed during the building of nets shows itself particularly, (Fig. 19, p. 16), because these interlink the chains by primary bonds and therefore are not loosened by the increase of temperature.

The above considerations will make it clear that the nature of the secondary forces between the side groups determines whether or not a substance possesses rubberlike properties at room temperature.

From Table 17 it appears that for rubbers the specific molar cohesion is between 1 and 2 kcal, whereas for fibres it is > 5 kcal. Substances with a cohesion between 2 and 5 kcal are more or less intermediate; they form the group of plastics although some of them can also be used as fibres. An exception

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[1] Which actually does take place (See page 40, footnote 1), but can be neglected as a first approximation, being relatively small.

is polyethylene; the fact that it is not a rubber although the cohesion is only 1 kcal is explained by the extraordinary crystallizing capacity, which can be readily understood by considering the symmetry of the monomer. Here none of the causes which might lead to irregular chains (page 13) is acting. Apart from this crystallizing capacity, the rotational possibilities of the chain elements with regard to each other also play a part.

TABLE 17.

SECONDARY AND PRIMARY BONDS IN SOME POLYMERS RELATED TO THEIR MECHANICAL BEHAVIOUR [1]

Substances	Covalent bond along chains	Dissociation energy cal/mole	Groups, responsible for attraction	Molar Cohesion per 5 Å chain-length with coordination Nr. of 4 in cal/mole
Polyethylene	—C- -C—	70-80,000	(CH_2)	1,000 plastic
Polyisobutylene	—C—C—	70-80,000	(CH_2), (CH_3)	1,200 rubber
Polybutadiene	—C=C—	70-120,000	(CH_2), $(CH=CH)$	1,100 rubber
Natural rubber	—C=C—	70-120,000	(CH_2), $(CH=CCH_3)$	1,300 rubber
Polystyrene	—C—C—	70-80,000	(CH_2), (C_6H_5)	4,000 plastic
Polychloroprene	—C=C—	70-120,000	(CH_2), $(CH=CCl)$	1,600 rubber
Polyvinyl chloride	—C—C—	70-80,000	(CH_2), $(CHCl)$	2,600 plastic
Polyvinyl acetate	—C—C—	70-80,000	(CH_2), $(COOCH_3)$	3,200 plastic
Polyvinyl alcohol	—C- -C—	70-80,000	(CH_2), $(CHOH)$	4,200 plastic
Cellulose	—C—O—C—	80-90,000	(OH), $(—O—)$	6,200 fibre
Cellulose acetate	—C—O—C—	80-90,000	$(OOCCH_3)$, $(—O—)$	4,800 plastic
Polyamides	—C—N—C—	70-90,000	(CH_2), $(CONH)H$	5,800 fibre
Silk fibroin	—C—N—C—	70-90,000	(CHR), $(CONH)H$	9,800 fibre ·

A further point, determining whether a material will be rubbery or not, is the entropy of fusion. According to MARK, for rubbers this entropy should be > 0.9 cal/°C/mole.

It ought always to be possible, however, to call forth the high elastic state by suitable heating. For this purpose as much heat energy should be supplied to the side groups as will sufficiently loosen the secondary cohesion. The temperature at which this occurs is the high elasticity temperature. It may therefore be said that the high elastic state is something between the liquid state (perfectly free macro-BM) and the solid state (macro-BM entirely prevented).

g. Plastic properties.

The plastic properties make their appearance only after the yield value has been surpassed and one may study them with the aid of the tension-elongation diagram (Fig. 26, p. 31). More suitable, however, is the flow process,

[1] H. MARK, *Ind. Eng. Chem., Ind. Ed.*, 34 (1942) 1343.

in which the rate of flow[1] D is determined as a function of the shearing stress τ. If proportionality exists, so that

$$D = \frac{\tau}{\eta} \quad \ldots \ldots \ldots \ldots \ldots \ldots (8)$$

one is concerned with pure or Newtonian flow, η, expressing the viscosity coefficient. For most polymers this is not true and usually (often after sur-passing the yield value) a relation of the type (9) is found:

$$D = \frac{\tau^n}{\eta} \quad \ldots \ldots \ldots \ldots \ldots \ldots (9)$$

where n measures the amount of deviation from the Newtonian law. Fig. 34 exhibits the two cases mentioned.
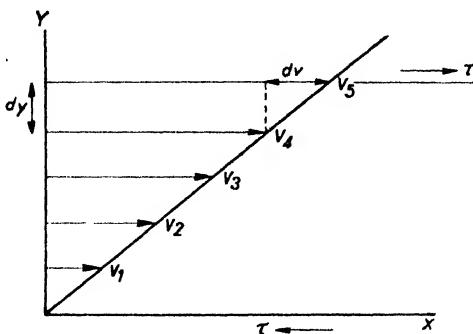
Fig. 33. Laminar flow.

The viscosity and the flow-limit are of very great importance in this flow-process, because they determine beforehand whether the forming process, which plastics must often undergo in the factory, will proceed easily or not. Most plastics have such a great viscosity at room temperature ($> 10^{10}$ poises) that deformation practically cannot be effected. Instead, we take advantage of the great temperature sensitivity of the viscosity, which is expressed[2] by the formula:

$$\eta = A e^{E/RT} \quad \ldots \ldots \ldots \ldots \ldots \ldots (10)$$

where $\begin{array}{l} A = \text{a constant} \\ E = \text{activation energy of flow.} \end{array}$

η diminishes roughly by one order of magnitude per $10°$ C increase of temperature. Thanks to this favourable circumstance it appears that by raising the temperature to between 100 and $160°$ C, most of the plastics are mould-

[1] D is the velocity gradient dv/dy in Fig. 33, showing laminar flow under influence of a shearing stress τ.
[2] T. ALFREY, *Mechanical Behavior of High Polymers*, New York 1948, page 74.

able [1]. This upper temperature limit has been adopted generally, so that conversely, we may say that a new plastic will find acceptance easily, only if the temperature at which it can be worked is not higher.
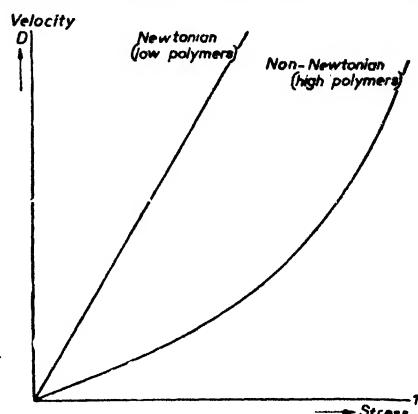

Fig. 34. Two frequently occurring types of flow in polymers.

h. Influence of the orientation.

When in a chain polymer a preferential direction is given to the molecules, it is understandable that the material acquires other properties in that direction. This can best be demonstrated with the material in the form of a film. In Fig. 35 are shown the tension-elongation curves for cellophane (cellulose regenerated from cellulose xanthate) parallel and perpendicular to the direction orientation. It appears that in the direction of orientation the strength is
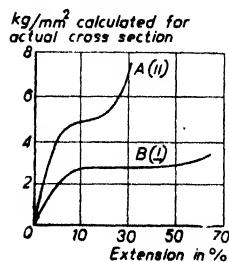
Fig. 35. Stress-strain diagrams of orientated cellophane in the two principal directions.
A. Substance // to the orientation direction
B. Substance ⊥ to the orientation direction.
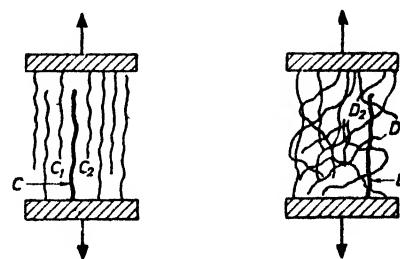
a. Parallel oriented   b. Unoriented

Fig. 36. The strength of the oriented fibres is greater than that of the disordered ones.

TABLE 18.

THE DEPENDENCE OF THE STRENGTH OF NATURAL SILK ON THE DEGREE OF ORIENTATION

Treatment of the silk:	Degree of orientation:	Strength in kg/mm^2
1. Not treated	very considerable	27
2. Dissolved and spun with little orientation	moderate	9
3. As under 2, but spun without being stretched	very small	0.3
4. As under 2, but strongly orientated	extremely great	40

[1] Cf. for the heat distortion points, expressing the temperatures at wich the polymers soften : Table 25, pg. 83.

considerably greater, but that on the other hand the elongation at rupture is much smaller than in the perpendicular direction. In general, for a certain elongation, in the direction A, a greater tension is required than in the direction B; consequently the material is harder (stiffer) in the A direction. To explain this, we refer to Fig. 36, in which a certain fibre C in the orientated material, on pulling the clamp, is supported along its entire length by the neighbouring fibres C_1 and C_2, whereas the fibre D touches D_1 and D_2 only here and there . Therefore, D glides away much easier, i.e., the resistance (measuring the modulus) and the strength are small.

It is just this possibility of orientation (combined with crystallization, see below) which has created useful artificial fibres and films, because these all possess long chain molecules, showing however only slight strength in the unorientated state. They do not reach their full strength until they have been stretched during the process of manufacture; in connection with rayon (p. 208) we shall consider this question more thoroughly. It is remarkable that as regards natural fibres the situation is exactly the same, and if the order created by nature is distorted the fibre immediately loses its strength. This is illustrated in Table 18 by some figures of VON WEIMARN [1] who dissolved natural silk, orientating it at will in the spinning process. It appears that the strength, according to the degree of stretching, varies from 0.3 to 40 kg/mm [2].

From this it becomes clear that it is useless to manufacture threads or films from polymers with only short chain molecules or round particles, because the surface of contact of the structural units will be too small to give a suitable strength.

Naturally the orientation shows itself also in the optical, röntgenographic and other physical properties; for the practical applications, however, this is less important and therefore we shall not go into it further.

Summarizing, the following appropriate connection was given by MARK [2] between the properties of polymers and their structural characteristics (Table 19). Typical thermosetting plastics and strongly vulcanized elastomers are not included in the discussion.

i. Influence of crystallization.

A further question of outstanding importance in determining the character of a material is the capacity to crystallize, already discussed earlier. A perfect crystalline lattice means that the side groups of the chain molecules have the opportunity of snapping into each other's potential troughs. This implies a great strength, but on the other hand a small extensibility; these two factors are precisely those necessary for *fibres*. In the case of rubbers a long range

[1] J. ALEXANDER's *Colloid Chem.* 4 (New York 1932).
[2] H. MARK, *Ind. Eng. Chem.*, Ind. Ed. 34 (1942) 1343.

TABLE 19.

APPROXIMATE CONNECTION BETWEEN PROPERTIES AND STRUCTURAL CHARACTERISTICS

Property	Average polymerization degree	Branching	Cross linking	Homopolar nature	Heteropolar groups	Flexibility of chains	Readiness of chains to crystallize	Orientation of crystallites
Modulus of elasticity	+	?	+	?	?	——	+	+
Ultimate tensile strength	+	?	?	—	+	?	+	+
Ultimate impact strength	+	?	—	+	?	+·	—	- —
Elongation to break	+	?	—·	+	?	·+·	—	—
Range of elastic extensibility	+	——	- —	·+	?	+	?	?
Tendency to contract	·+·	?	—	+	—	·+	—	?
Surface hardness	·+	?	+	- —	+	—	+	·+·
Resistance to temp.	+	?	+·	—	+	—	·+·	?
Electric resistance	?	?	+	+	—	?	?	?
Dielectric constant	?	?	?	—·	+	?	?	?
Resistance to swelling	+	+	+	?	?	—	+	+
Resistance to moisture	+	+	+	?	?	—	+	+
Resistance to acids and alkalis	?	?	+	+	?	?	+	?
Adhesive power	?	+	—	?	+	+	—	—

A plus sign means that the structural feature increases the property under consideration; a minus sign means that it decreases it. A question mark indicates that we do not know how the property is affected by the structural characteristic.

extensibility, combined with a great strength in the stretched condition, is wanted. This means that the material should be amorphous in the initial condition, but crystalline after stretching. This can be observed in a good rubber like the natural product having regular chains, in contrast to poor rubbers like GRS which possess irregular chains. The plastics occupy an intermediate position having no strong crystallizing tendency. This means that they are easily deformable in any state of stretching.

§ 15. THERMAL BEHAVIOUR

It is clear, that the properties of a polymer (especially thermoplastics) are influenced in a very peculiar manner by the temperature. This is able to be explained from the fact that the energy content of the secondary bonds is of the order ot KT, so that a change in the latter by raising T makes itself felt in the secondary cohesion but not in the primary cohesion which is so much richer in energy.

By measuring the change of some physical property — like the density — on cooling a polymer, a curve of the type in Fig. 37b is observed, where T_s and T_f indicate the temperatures of the solid and the fluid state, respectively. In contrast to Fig. 37a, where a sharp transition is found for crystals, a long melting range is observed for polymers, — the *transformation interval*.

In this transformation interval there is a region of rubbery elasticity; its temperature range depends on the kind and the length of the macromolecules. The explanation of the difference from crystals is that in the latter all

a. In crystals.   b. In polymers
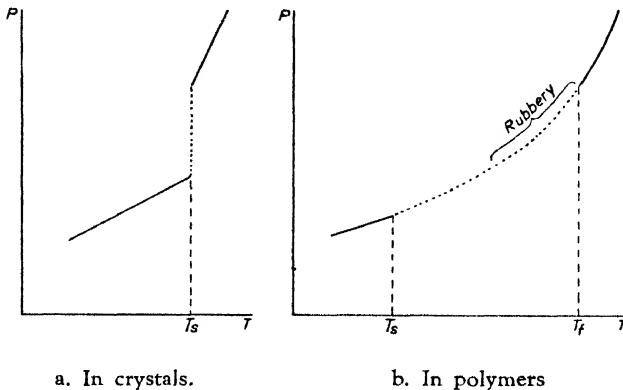
Fig. 37. The transformation interval.

forces between the atoms are of the same energy content and thus are all broken at a certain temperature. In polymers, however, there are secondary forces of different strengths and there are molecules of different lengths, so that a whole range of temperatures has to be passed from the loosening of the most easily melting molecules (T_s) to the highest melting molecules (T_f).

This explains why the *softening temperature* even for a fixed polymer is not a sharply defined point. It depends on the criterion used to define the softening, that is, on the type of apparatus employed in measuring it. With a thin needle one finds a different softening temperature than that found in compression between parallel plates. Comparisons should therefore always be carried out using the same method of testing.

We refer to Table 25 (page 83) in which a comparison of the softening temperatures is made for various polymers. The fundamental difference between the thermoplastics and the thermosetting materials, however, can also be made clear from a comparison of the tensile strength diagrams, as is demonstrated by Fig. 38.

At — 80° C the strength of both groups of materials is at least between 500 and 900 kg/cm². For the thermoplastics it has come down in all cases to below 300 kg/cm² at 80° C, but for the thermosetting materials a temperature of about 150° C is necessary for such a reduction.

It is interesting to note that for most materials on increase of temperature there occurs first an increase of the impact resistance (a measure for the toughness, see page 38), later a decrease can be observed. The maximum
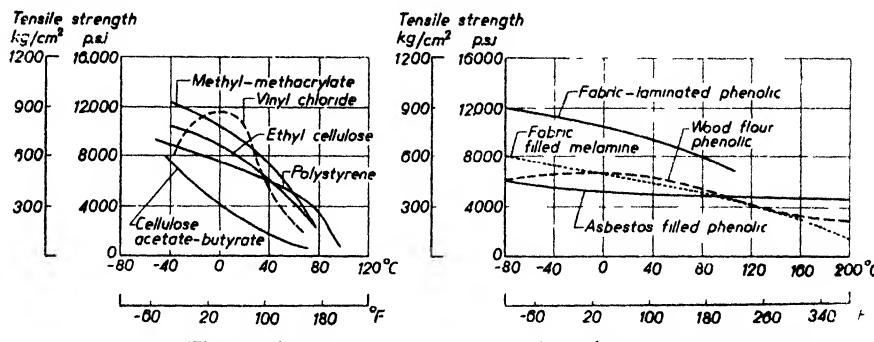
a. Thermoplastics.   b. Thermosetting materials.

Fig. 38. Influence of temperature on tensile strength [1].

corresponds to the more or less rubbery state of the materials which is effected by heating.

We have already discussed the stopping of the micro-Brownian movement leading to solidification at T_s. At a certain temperature the polymer becomes hard, but it is impossible to say as yet exactly what occurs at that moment [2]. It may be that all micro-Brownian motions come to a standstill; it is also possible that only part of them are stopped. A complete stoppage would correspond to what is scientifically called the *second-order transition point*, T_m. The temperature at which the brittle state begins is called the *brittle point*, T_b. It is impossible to say exactly where T_s, T_m and T_b lie, because none of them is exactly defined and each of them depends on the method by which it is measured. In Table 20 T_m and T_b are listed for some polymers.

TABLE 20.

SECOND ORDER TRANSITION POINTS AND BRITTLE POINTS

	T_m		T_b	
	°C	°F	°C	°F
Polyisobutylene	—74	—102	—50	—58
Natural rubber	—73	—100	—58	—74
Polyvinylidene chloride	—17	2	—	—
Polyvinyl acetate	28	82	—	—
Nylon	47	116	—	—
Cellulose nitrate	53	128	—	—
Polyvinyl chloride (hard)	75	167	81	176
Polyvinyl alcohol	85	185	—	—

[1] T. S. CARSWELL and H. K. NASON, *Modern Plastics*, 21 (1944) 121.
[2] See for this complicated subject: R. F. BOYER and R. S. SPENCER in *Advances of Colloid Science*, Vol. II, New York 1946, p. 1.

It appears that, roughly speaking, the harder materials have a lower value of T_m. On page 144 we shall again deal with the brittle temperature in connection with the rubbers.

Among the thermal properties, the *heat-expansion* should also be mentioned. In general it may be said that the thermal expansion is smaller for primary than for secondary bonds. For substances with oriented chain molecules the expansion will therefore be the smaller one in the direction of orientation; low-polymer substances will have a great heat expansion because they possess only a few primary bonds.

§ 16. SOLUBILITY AND SWELLING

During dissolution of a substance an initial swelling, i.e., a penetration of the solvent, invariably takes place. It is important to determine whether this process is limited or not.

The question as to whether high polymers are soluble or liable to swelling is especially important in determining their applications. Solubility is often desirable because then application as a lacquer is possible, but, on the other hand, the swelling-capacity may be highly undesirable because this gives the opportunity for solvents to penetrate.

Let us consider the energy interactions between the polymer and the solvent molecules [1] by starting from two liquids. These will mix as long as a decrease of free energy is involved. The second GIBBS law states that

$$\triangle F = \triangle U - T \triangle S \ldots \ldots \ldots \ldots \ldots \ldots (10)$$
where F = free energy, U = internal energy, S = entropy.

Hence liquids will only mix when $\triangle F$ is negative, that is, when $\triangle U$ is negative or when $T \triangle S > \triangle U$.

Consequently, there are two factors controlling $\triangle F$: the change in internal energy and the change in entropy. The entropy is always striving to reach a maximum and thus $T \triangle S$ is always positive, making $-T \triangle S$ negative. *Solution is therefore always promoted by the entropy factor* and it depends only on the magnitude of $\triangle U$ whether or not solution occurs.

In considering $\triangle U$ more closely, it must be realized that for dissolving, two molecules of the polymer, as well as some solvent molecules, must each time be separated from each other in order to create the conditions necessary for a contact between these polymer and solvent molecules.

This energy has to be added to the system. On the other hand, energy is liberated when the solvent molecules enter into contact with the polymer

[1] For general considerations about these problems see G. GEE, *Trans. Faraday Soc.*, **38** (1942) 276, 418.

molecules. It is the arithmetic sum of these two energies which controls the final result (the entropy factor is neglected here). One can thus split $\triangle U$ into two parts as follows [1].

$$\triangle U = -U_{LP} + (U_{LL} + U_{PP}) \dots\dots\dots\dots (11)$$

where $\triangle U$ = heat development on swelling

       U_{LP} = interaction between 1 mole of liquid and one mole of the polymer

       U_{LL} = energy to remove one mole of liquid from its neighbours

       U_{PP} = energy to separate two moles of the polymer.

If $\triangle U$ is negative, i.e., if U_{LP} is so important that heat is finally liberated, then solvent molecules enter into the polymer, which then starts swelling. It is a further question, whether the swelling will change into complete solution (see below). The entropy factor is thus promoting solution and one can conclude that for a negative $\triangle U$ all conditions for solution are favourable.

If $\triangle U$ is positive, however, i.e., if $(U_{LL} + U_{FP})$ is the dominating factor, then the situation changes; from the point of view of energy no solvent molecules can enter into the polymer. Only if the entropy factor is sufficient to overcompensate this positive $\triangle U$ will solution take place. It appears that this situation is often encountered; many polymers only dissolve because of the important gain in entropy, $\triangle U$ being slightly positive in many cases (e.g., for rubber in benzene). A striking example of the importance of these considerations is that rubber dissolves in benzene, whereas gutta, having a larger $\triangle U$ due to its crystallization, is insoluble in benzene. In such cases a small increase in temperature may suffice for solution, increasing the value of $T \triangle S$ (see polyethylene, page 108).

Now the question arises as to when the swelling will remain limited and when it will change into a complete solution process. To determine this, let us consider a copolymer with groups of different polarity, which are designated as K_1 and K_2 (Fig. 39). We suppose, for example, that the groups K_1 are dipoles and K_2 benzene rings; the latter exercise only dispersion forces on each other.

We can now imagine that a solvent will be able to separate the K_2 groups from each other, but not the K_1 groups. Thereupon a situation arises as represented in Fig. 39b, which is characterized by the ability of the solvent molecules to bend apart the chains only partly; this is an example of limited swelling.

By changing the degree of polarity in the chain, this may result in the polymer becoming soluble in a liquid in which it was hitherto insoluble. Referring

[1] K. H. MEYER, *Natural and Synthetic High Polymers*, New York 1942.

to Fig. 39b, it will be clear that by decreasing the number of K_1-groups a nonpolar liquid becomes a better solvent.
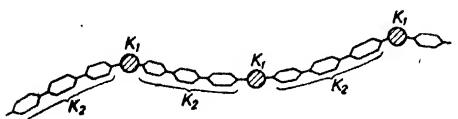
a. Chain molecule with polar K_1 groups and non-polar K_2 groups.
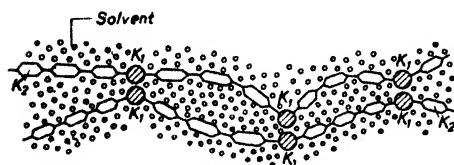
b. The swelling process.

Fig. 39. Explanation of the restricted solubility (swelling), due to the action of dipoles K_1. If the K_1—K_1 bonds were primary bonds (interlinking), a similar situation would arise.

An interesting example [1] of this is ethylcellulose, where the degree of etherification is decisive for the kind of solvent and for determining whether actual solution or only swelling occurs. The more (polar) OH-groups are etherified, the less polar is necessary for the solvent to be (see Table 21).

TABLE 21.

INFLUENCE OF THE DEGREE OF ETHERIFICATION OF
CELLULOSE ON THE SOLUBILITY

Degree of etherification	Solubility
0.5 ethoxygroups per glucose unit	Soluble in alkali solutions
0.8-1.3 ,, ,, ,, ,,	Soluble in water
1.4-1.8 ,, ,, ,, ,,	Soluble in polar and non-polar solvents.
2.2 ,, ,, ,, ,,	Soluble in organic solvents, but solutions show granular flow.
2.4-2.5 ,, ,, ,, ,,	Maximum solubility.
2.5-3.0 ,, ,, ,, ,,	Rapid drop in solubility in alcohols; becomes soluble only in non-polar solvents

Between 1.4 and 2.5 ethoxy groups per glucose unit, the balance between polar and non-polar groups is such that most solvents are capable of disturbing all secondary bonds. When either the amount of polar or the amount of non-polar groups is preponderant, this is not possible.

It is clear that limited swelling always occurs in the case of interlinking because this means nothing more that the dipole bond, indicated in Fig. 39

[1] D. TRAIL, Ethyl Cellulose and Benzyl Cellulose. Plastics Monographs No. 8, London 1945.

as K_1K_1, is replaced by a primary bond of very high energy content. A characteristic example of limited swelling has been described by STAUDINGER [1] for polystyrene interlinked by means of p-divinylbenzene, according to Fig. 40. The bridges in this figure have been shaded. The value of this experiment

$$.. - CH-CH_2 \quad CH_2-CH_2 -\left(CH-CH_2\right)-CH -CH_2-CH-CH_2-CH-CH_2-..$$

$$.. - CH-CH_2-CH-CH_2-\left(CH-CH_2\right)-CH-CH_2-CH-CH_2-CH-CH_2..$$

$$...-CH-CH_2-...$$
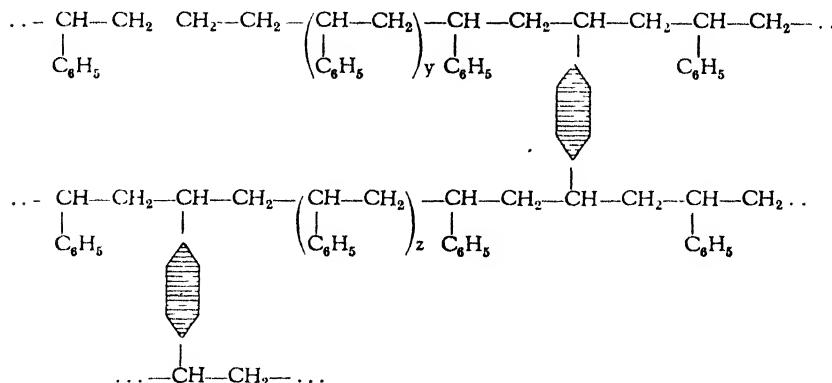
Fig 40. Interlinking of p-divinylbenzene between polystyrene chains. The benzene groups of the divinylbenzene which form bridges have been shaded.

is that we learn how few bridges are necessary to arrive at a strictly limited capacity for swelling. Fig. 41 shows (to the right) a tablet of the unswollen material with 0.01% divinylbenzene; to the left the same tablet is represented after the swelling in benzene. It must be pointed out that such an important influence of so little impurity (0.01%) can only be explained by the high molecular structure of the polystyrene, because it is only then that one mole of divinylbenzene suffices to bind many base moles of styrene.

Fi. 41. Swelling of polystyrene in benzene with 0.01% of divinylbenzene.

[1] H. STAUDINGER, Trans. Faraday Soc., 32 (1936) 323.

HERMANS [1], taking into consideration Fig. 42, stresses the point that the swelling process is accompanied by rather complicated phenomena. The network elements must be stretched so that in a gel swollen to its maximum we shall find stretched molecules. During the contraction these must fold in again.

a. Before swelling.   b. After swelling.

Fig. 42. Elongation of the net elements during swelling.

In cases where we have solely to do with chain molecules, one would be inclined to suppose that when the monomer can be dispersed into a solvent the polymer will also be soluble therein. However, this is not always the case because the solubility decreases as the molecular weight increases, according to the equation: [2]

$$\frac{Cp}{C_P} = e^{(P-p)/E} \quad \ldots \ldots \ldots \ldots \quad (12),$$

where Cp and C_P are the concentrations of the low and high molecular constituents, respectively; E = heat of solution per mole of structural units.

This equation gives the distribution of the solvent between two fractions, the degree of polymerization of which are P and p, respectively ($P < p$). Such an influence of molecular weight on the solubility is demonstrated by the low molecular paraffins in Table 22.

TABLE 22.

THE SOLUBILITY OF PARAFFINS DECREASES WITH
THEIR MOLECULAR WEIGHT.

	Solubility in water (10^{-4} mole/liter)
$C_5 H_{12}$	50
$C_6 H_{14}$	16
$C_7 H_{16}$	5
$C_8 H_{18}$	1

The limit between solubility and insolubility is not sharp; there is a small transitional domain where the substance dissolves only partially, in other words, only swells. From the equation (10) it may be inferred that by increase of temperature substances which swell can be brought into solution.

[1] P. H. HERMANS, Kolloid-Z., 96 (1941) 311.
[2] K. H. MEYER, Natural and Synthetic High Polymers, New York 1942.

Regarding the *wetting of pigments* by liquids, essentially the same considerations are valid as developed on page 50 for the interaction between liquid and polymer. A difference may be that in many cases the pigment particles are much coarser than the polymer molecules but there are cases where the order of magnitude is the same. Carbon black particles usually have a diameter of 500—1000 Å (50—100 mμ) and at present kinds with a diameter of 300 Å are marketed. The order of magnitude for some micelles is about 100 Å (see page 30). Such fine pigment particles possess a surface area of 500 m² per cm³ (1 cm³ = 1.8 gram).

In polymer technology one has to deal with two different ways for wetting this large pigment surface. One is by using a solvent (lacquers) which dissolves the polymer and wets the pigment at the same time. After evaporation, the polymer replaces the solvent, entering into contact with the pigment particles. Another way (dry method) is for the polymer in fluid or plastic condition immediately to enter into contact with the pigment (compounding of rubber). In either case the final interaction between polymer and pigment is decisive for the technical result. For this interaction one can write an equation like (11) in which L has to be replaced by p (pigment).

§ 17. THE PROPERTIES IN SOLUTION[1]

For polymers in solution, the viscosity is the most important physical constant and, as a rule, measurements are made of the change of η with concentration. According to the rule of EINSTEIN, the viscosity of dilute solutions or suspensions of globular rigid particles depends solely on the part by volume of the dispersed substance, but is independent of the dimensions of the particles:

$$\eta_r = 1 + KC_v \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (13)$$

where η_r = relative viscosity = $\dfrac{\text{flow-time of the solution}}{\text{flow-time of the solvent.}}$;

C_v = concentration by volume; K = constant.

The constant K therefore is decisive for the increase of viscosity of the solution and consequently is sometimes designated as the *viscosity constant* or *intrinsic viscosity*[2].

On further examination[3] K may be separated into two factors, viz:

$$K = DV_0 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (14)$$

V_0, the "voluminosity", is the actual volume which the particles, in conse-

[1] See for a recent survey: R. H. EWART, *Advances in Colloid Science*, New York 1946, p. 197.

[2] The relation holds good only in the case of infinite dilution, so that $K = \left(\dfrac{d\eta_r}{dc_v}\right)_{c_v} \to 0$.

    K is denoted in the literature as $[\eta]$; W. PHILIPPOFF, *Die Viskosität der Kolloide*, Dresden 1942.

[3] R. HOUWINK and K. H. KLAASSENS, *Kolloid-Z.*, 79 (1937) 138; 99.

quence of swelling, etc., occupy in the solution. D is a factor which indicates how much energy is transformed into heat during the flowing; for round particles D is 2.5; for oblong particles D is larger.

On the basis of this concept, there would appear to be two factors which lead to an increase in viscosity: (1) the swelling of round particles and (2) the deviation from the ball-shape. These two factors play an important part because of the preponderance of large particles in polymers. If they are ball-shaped they can swell, and this will depend on the degree of interlinking — the more interlinking the less swelling (see the considerations of page 52). If the particles consist of chain molecules, they may be in the stretched form or coiled up into balls. In the latter case, one is again concerned with round particles or coils, as in Fig. 43c. The important point here is the "voluminosity" (V_0) of the clews, that is, the extent to which they are swollen. V_0 is a measure of the looseness of the swollen clews. Fig. 43 gives[1] a picture of a polymer at different concentrations in good and in bad solvents.

There exists here a complex of questions regarding which there is much to do in the literature. STAUDINGER has from the beginning defended the form of rods of the chain molecules and previously even supposed them to be rigid. This idea has now been abandoned but, notwithstanding this, the so-called viscosity law of STAUDINGER can be used for the determination of the molecular weight of polymers (see page 68).
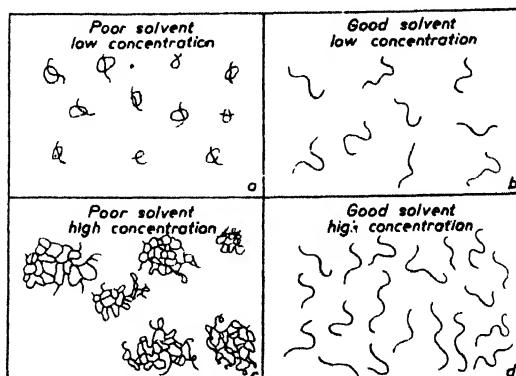
Fig. 43. Dissolved polymer molecules.

It is remarkable that the most voluminous coiled particles, which in low concentration give the greatest contribution to the increase of viscosity, increase the viscosity relatively less in high concentrations. This is explained by the supposition that with higher concentrations the more voluminous particles form a close packing sooner. They are then more easily compressed on increasing the concentration, their voluminosity becoming smaller.

[1] After A. G. JANSSEN and B. P. CALDWELL, Polymer Bull., 1 (1945) 120.

With compact particles, however, such a compression will take place to a smaller extent.

From the above it appears that polymers form solutions of high viscosity when they are dispersed either as stretched molecules or as molecules wound loosely into a coil. This is often a disadvantage because in the greater part of the practical applications (lacquers), low viscous solutions of a high concentration are desirable. In order to attain this, we avail ourselves of an artifice. Most polymers can be emulsified, which means that small globules (each containing millions of molecules of the polymer) are dispersed in a liquid like water. In these drops the chain molecules lie closely packed so that the voluminosity becomes equal to 1. Moreover, the drops are round, so that the factor D in (15) is reduced to its minimum: 2.5. Consequently, η_r then has the lowest possible value.

§ 18. SOFTENING AND PLASTICIZING[1]

Swelling in a solvent always causes a softening of the polymer and very frequently this is denoted as plasticizing. This name is often wrong because in many cases the material becomes more highly elastic on swelling (compare a gelatine pudding with dry gelatine). Strictly speaking one should therefore distinguish between plasticizing and elasticizing, the name softening involving either or both of them.

One distinguishes between external and internal softening as follows.

a. *External softening* involves the action of solvents (already described). Usually, first an elastification takes place, but after surpassing a certain content of solvent the material begins to flow more easily; then the plasticizing begins. The conditions for *external softening* are therefore fundamentally the same as for dissolving, it being necessary to surround the molecules of the polymer with solvent molecules. The only further condition is that the boiling point of the softener is high, because otherwise it would evaporate too quickly. It is not necessary that polymer and solvent are completely miscible; compatibility must only exist in the proportions necessary to obtain the desired effect in the temperature range involved. Fig. 44 shows[2] a typical example for cellulose acetate and dimethylphthalate as plasticizer. Here the region of incomplete miscibility is far removed from the regions of practical application so that no danger exists that the plasticizer will be squeezed out.

In Fig. 45 another presentation[3] is given for the properties: solubility,

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[1] See for a comprehensive treatment of plastification: P. B. STICKNEY and L. E. CHEYNEY, *J. Polymer Sci.*, 3 (1948) 231.

[2] H. M. SPURLIN, A. F. MARTIN and H. G. TENNENT, *J. Polymer Sci.*, 1 (1946) 63.

[3] R. W. QUARLES *Ind. Eng. Chem.*, 35 (1943) 1033.

fluidity, thixotropy [1] and gel formation. The mixture contains one polymer (copolymer of vinyl chloride and vinyl acetate), one solvent (acetone) and one diluent (toluene). On the ordinate the resin content of the final mixture is plotted against the solvent content and the curves represent the
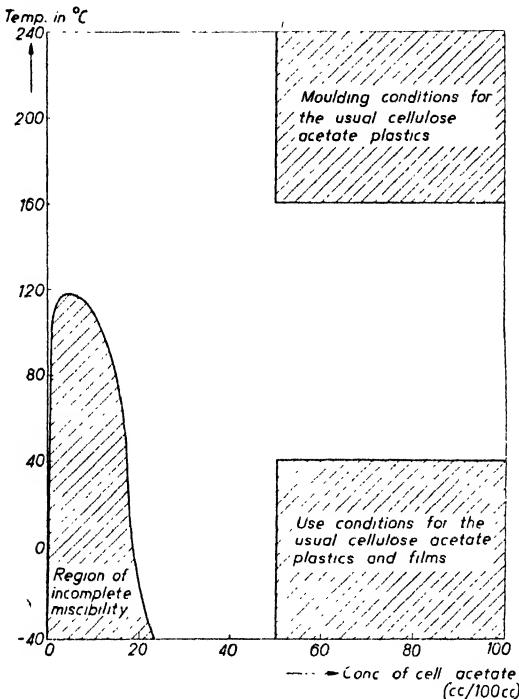
Fig. 44. Temperature-concentration relationship for cellulose acetate, plasticized with dimethyl phthalate.
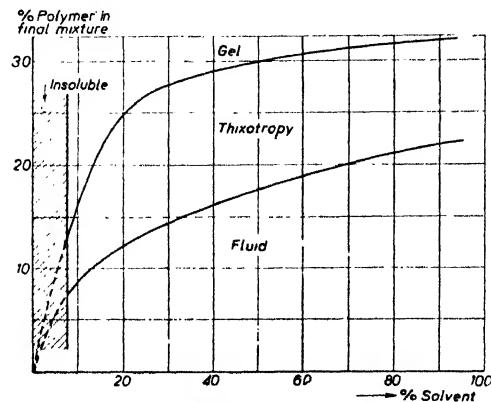
Fig. 45. Limiting concentrations, at which a mixture of vinylite, acetone (solvent) and toluene (diluent) develop certain rheological characteristics.

[1] Thixotropy means that a substance is a gel when at rest, but becomes fluid on stirring. It is intermediate between the fluid and the solid state.

limiting concentrations at which the solution develops the characteristics mentioned in the illustration.

Below 5%, acetone insolubility exists; the higher this percentage, the higher the polymer content can be for a certain fluidity. Diagrams of this type are extremely important for the paint and varnish industry.

The softening action can also be demonstrated by means of the second
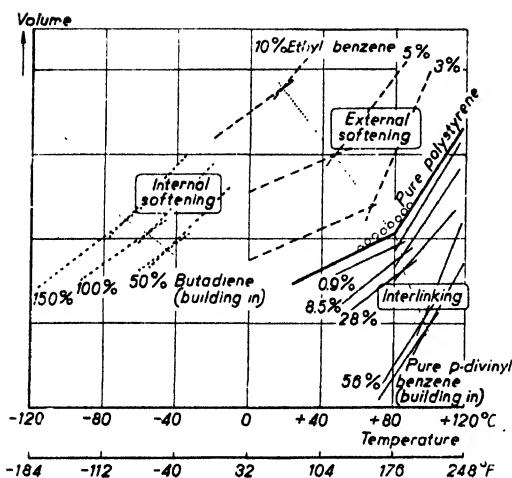
Fig. 46a. Softening (internal and external) and stiffening of polystyrene.
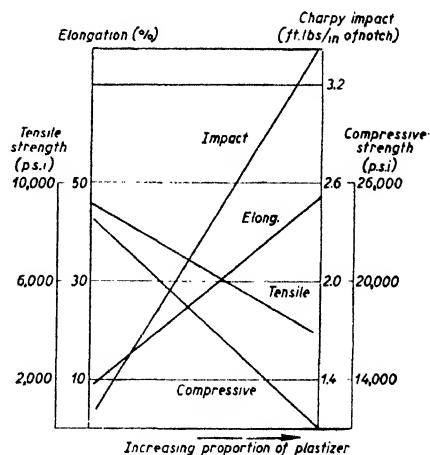
Fig. 46b. Effect of external plasticizing on phycical properties of cellulose acetate.

order transition effect, mentioned on page 49. Measuring the decrease of volume on cooling a polymer, the curve shows a sudden change of direction at a certain temperature; for polystyrene this occurs at about 80 °C (176 °F), see Fig. 46a. At this temperature the polystyrene "freezes". It is probable that above 80° C many chain elements are still mobile (micro-B.M., see page 40). Therefore the molecule occupies a relatively important volume, but at 80° C these elements usually come to a standstill and below this temperature only a little swinging of single atom groups will take place.

In Fig. 46a, the curves, fully extended, indicate how the freezing temperature during the building-in of p-divinylbenzene as a bridge between the chains (see Fig. 40, page 53) increases. On the other hand the dotted lines show that when adding ethylbenzene as a softening agent, the freezing temperature decreases. All this can be understood easily; increasing amounts of p-divinylbenzene bind up the chains more and more, so that higher temperatures are necessary to loosen them again. Softening agents on the contrary reduce the cohesion.

In Fig. 46b the effect of plasticizer on the physical properties of

cellulose acetate is presented[1]. It appears to be quantitatively proportional to concentration. Attention is drawn to the fact that the tensile strength decreases, whereas the impact resistance increases, a generally observed phenomenon, when plasticizing.

b. *Internal softening* is brought about by building the softening agents *into* the chains instead of adding them as a solvent. An example of this is shown in the curves for the copolymer styrene-butadiene with increasing proportions of butadiene (Fig. 46a). It appears that the transition point also shifts to the left, just as happens when adding the solvent ethylbenzene. Butadiene is a gas whose molecules attract each other very little, and thus the loosening effect on the total cohesion can be understood.

§ 19. OPTICAL AND X-RAY BEHAVIOUR

Among the optical properties of polymers, the *transparency* is of great importance. When unfilled, the vinyl polymers (polystyrene, polyacrylic derivatives) are transparent like glass, so that they can be used for optical purposes.

The *refractive index* lies, as a rule, between 1.4 and 1.6 and increases as the degree of polymerization increases. This is connected with changes in the density.

The study of *double refraction* has, in many respects, thrown much light on the structure of polymers. By means of these phenomena it can be ascertained whether a substance possesses round particles or not, since by orientation of oblong particles double refraction results, i.e., the material becomes anisotropic.

The lack of such anisotropy furnishes one of the most important proofs for the ball-shaped molecular structure of the phenol-formaldehyde resins. [2]

Still more than the optical research, *X-ray* investigations have contributed to the elucidation of the structure of high polymers. [3]

There are five main peculiarities of the structure which can be elucidated with the aid of X-rays:

1. whether a substance is amorphous or crystalline;
2. whether in an amorphous substance during polymerization the dimensions of the structural unit change;
3. whether a crystallized substance is entirely crystalline or whether it only contains crystalline elements (crystallites, see page 30);
4. whether the crystallites are oriented (fibre diagram);
5. what the dimensions of the crystallites are.

---

[1] J. DELMONTE, *Plastics in Engineering*, Cleveland 1943, page 203.
[2] R. HOUWINK, *Phys. Eig. und Feinbau von Natur und Kunstharzen*, Leipzig 1934.
[3] A survey is given by C. W. BUNN in *Advances in Colloid Science*, New York 1946, p. 95.

In this way it has been possible to investigate the structure of the crystallized polymers (cellulose derivatives) and it has also been proved that other polymers can crystallize, while being stretched, (rubber). It has also been shown that during swelling an expansion of the lattice takes place and we may rightly say that without X-rays our knowledge of the structure of polymers would be quite incomplete.

§ 20. ELECTRICAL PROPERTIES[1]

From the very beginning, the electrical properties of the polymers have been in the spotlight because, in particular, the needs of the electrical industries have stimulated the development of many new materials. When, later on, it appeared that the electrical test could furnish valuable conclusions regarding theoretical questions, there developed what may be called a full-fledged electrophysics of high polymers. Only those items of interest in actual practice will be dealt with here. In technology we have principally to do with the circumstances set down in Table 23.

TABLE 23.

CHIEF RANGES OF USE OF POLYMERS IN ELECTROTECHNOLOGY

	Tension in Volts	Current in Amp	Range of frequencies in Hz
a. Weak current, low tension	up to 20	0.1—1	0—10
b. Strong current, low tension	100—300	> 0.1—1	50
c. High tension	3,000-200,000	10—100	50
d. High frequency	< 20	< 0.1—1	$< 10^5$

a.   Conductivity.

If atoms are brought into an electric field, the nucleus is shifted in one direction, the cloud of electrons in an opposite direction. The electrical tension can become so strong that the electrons are torn from the atom, thus creating an electric current. In most insulating materials, however, the electrons are tied so firmly that a current is produced in a different manner. Usually ions (impurities!) are present which can move through the field and cause a certain current at low tensions.

Therefore, in the majority of polymers *the conductivity depends on the amount and the constitution of the contaminating impurities* and on the viscosity of the medium; the degree of humidity plays an important part. In certain polymers

[1] See for a survey: R. M. Fuoss, in R. E. Burk and O. Grummitt, *The Chemistry of Large Molecules*, New York 1943, p. 191; L. Hartshorn, *Brit. Plastics*, 17 (1945) 99, 186; J. Granier and G. Granier, *Les proprietés électriques des résines synthétiques*, Paris 1948.

the number of free ions is so great, that they must be reckoned among the semi-conductors.

The specific resistance is expressed in ohm cm, which is equal to the resistance of a cube with a length of side of 1 cm. For the majority of polymers the specific resistance is between 10^{10} and 10^{15} ohm cm; Tables 25 and 26 give further information in this respect.

In practice one has not only to consider the conductivity of a material as such, but also the current-leakage over the surface, especially under wet conditions. Fig. 47 shows [1] this to be important not only for materials containing hygroscopic ingredients which can easily split off ions (wood flour in P.F. mixtures) but also for materials like polyvinyl chloride. Perhaps the splitting off of Cl-ions plays a part here.
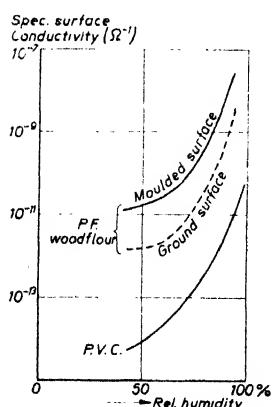
Fig. 47. Influence of moisture on the surface conductivity of moulded phenol-formaldehyde wood flour mixture and of polyvinyl chloride.

b. Breakdown Voltage.

It is now clear that the conductivity by alien ions will influence the breakdown voltage but for *good* insulators the tearing loose of the electrons will be decisive.

Exactly as was the case with the tensile strength (page 34), the experimental electrical breakdown limit also lies far under the limit, which theoretically may be expected. For good insulators the practical breakdown voltage is of the order of about 10 to 30 kV/mm. Much depends, however, on how the test is executed. A slow increase of tension results in a breakdown which is influenced by heat effects. This can be explained thus: as the current develops heat in consequence of the increase in temperature, the conductivity increases, and so on until an avalanche-like breakdown occurs. In contrast stands the momentary breakdown which occurs instantaneously if a sudden voltage is applied. This seems to be due to the immediate tearing loose of electrons. One might expect the breakdown voltage to be a physical constant, so that it might be expressed per centimetre thickness of material. This has not proved to be correct and, therefore, whenever breakdown voltage is mentioned, the thickness and also the manner in which the increase of tension took place should always be stated exactly.

[1] H. VIEWEG and H. KLINGELHÖFFER, Kunststoffe, 32 (1942) 77.

c.   *Dielectric losses and dielectric constant.*

Let us revert to the displacement of the nucleus and its electron cloud in opposite directions, as mentioned under *a*. It is then clear that when the atom is polarized an induced electric moment, m, comes into being, according to the equation:

$$m = \alpha V \dots \dots \dots \dots \dots \dots \dots (15)$$
$$\alpha = \text{polarizability, } V = \text{electric tension}$$

Here we recall to mind the dipoles, multipoles and induced dipoles, mentioned on page 26, which are present in many polymers. If the substance is brought into an alternating electric field, all these aforementioned polar spots are directed alternately to the + and to the — side of the field, so that they start swinging to and fro. Owing to the internal friction in the material, the movement of these groups is accompanied by a heat development according to the formula:

$$H = V^2 \omega \, \varepsilon \, C_o \, \text{tg } \delta \dots \dots \dots \dots (16)$$

where H = heat; ω = angular velocity of the tension vector; C_0 = air-capacity of the air condenser which has formed; V = tension; ε = dielectric constant; tg δ = phase angle.

These so-called *dielectric losses* must be furnished by the exterior field and hence it can be seen that, in general, a demand for material with low losses will exist.

In a purely formal way the situation can be expressed as follows: The dielectric losses are determined by the extent to which a dielectric deviates from the ideal state, in which the phase displacement between the tension and current vectors amounts to exactly 90° ($^1/_4$ period). If losses are present, a phase displacement appears over an angle δ, which is a measure of the losses and which is called phase angle; in practice tg δ is used.

Tg δ depends on the frequency, as the dipoles must be able to adjust themselves sufficiently rapidly in order to follow the alternating of the field. When the frequency of the micro-Brownian motions (page 40) is of the same order of magnitude as the frequency of the exterior field, tg δ becomes a maximum.

The technically important frequencies lie at 50, at 800 and at 10^6 respectively and the tensions which in practice occur in this connection have been summarized in Table 23. Tg δ, which varies in polymers between about 0.0001 and 0.1, is often expressed either as a percentage or in units of 10^{-4}. Tg δ = 0.01 therefore, sometimes is also indicated as tg δ = 1 $^0/_0$ or tg δ = 100. 10^{-4}.

The ratio between the charge E and the tension V of a condenser is called the capacity C and thus $C = \frac{E}{V}$. The *dielectric constant* ε of an insulating material is the factor by which the capacity of a vacuum condenser is increased, when the air is replaced by the insulator. This means that the current through

the condenser also increases by the factor ε when adjusting the insulating material. According to definition, ε is for vacuum (and therefore practically also for air) equal to 1; for good insulators, we find values between 2 and 5. The dielectric constant is in a very similar way due to the orientation of polar parts in the insulator. This is formulated by DEBYE as follows:

$$\frac{\varepsilon-1}{\varepsilon+2} = p_E + p_A + p_R + p_O \cdots \cdots \cdots (17)$$

Here p_E, p_A, p_R signify, respectively, the polarizations of electrons, atoms and radicals; p_O the polarization due to induced polarization (orientation polarization).

Like tg δ, ε also depends on frequency, but according to different laws, because ε is dependent on orientation only, whereas tg δ is only caused by rotation or oscillation. Where the frequency of the field reaches the order of magnitude of the mean frequency of a dipole, the dipole movement becomes strongest and, consequently, the dipole orientation becomes imperfect, i.e., ε decreases just when tg δ becomes important.

Fig. 48 shows very generally the way in which tg δ and ε should be connected with the frequency and also with the temperature. One finds here for tg δ, in
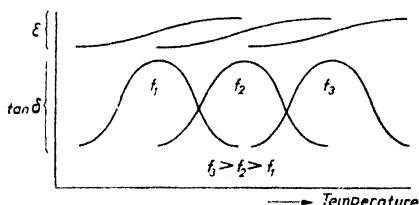
Fig. 48. Dielectric losses (tg δ) and dielectric constant (ε) for various frequencies as a function of temperature.

every range of frequencies, a maximum, which consequently proves that at that particular frequency the losses by friction due to the dipole mobility become greatest. That the temperature has a great influence on the dielectric properties is comprehensible when we bear in mind that the mobility of molecules and of groups of molecules and also the viscosity strongly depend thereon. The ideal curves of Fig. 48 are not always found in practice because many disturbing influences can appear.

In Fig. 49 a family of curves
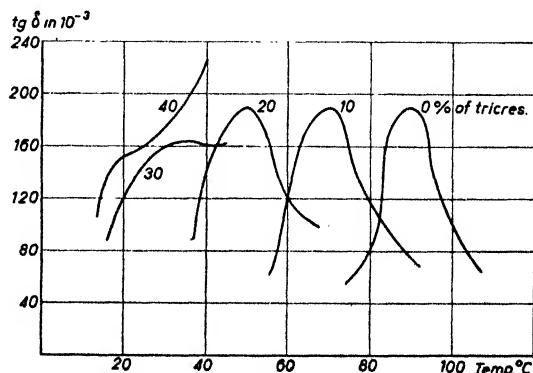
Fig. 49. Influence of temperature on polyvinyl chloride with various proportions of tricresyl phosphate.

from actual practice is shown [1] for polyvinyl chloride with various contents of tricresyl phosphate as plasticizer. Each curve has a maximum for tg δ at a certain temperature that is lower the more softener is present. This is according to expectation, because a certain amount of softener corresponds to a certain mobility of the dipoles. When adding more softener, the temperature has to be reduced to restore the same mobility.

§ 21. PERMEABILITY[2]

The *gas permeability* is for many polymers an important property on account of their use as lacquers or as inner tubes and packing materials. In order that a gas may permeate it must first of all dissolve in the polymer and then diffuse further. Therefore

$$P = Dh \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

applies[3], in which:

P = Quantity of permeated gas (permeation coefficient) in $\dfrac{cm^3.\ cm}{cm^2.\ sec.\ atm}$

D = Diffusion constant in cm^2/sec

h = Solubility constant [4]

Further it is found that P increases with the temperature according to the formula:

$$P = Ae^{-B/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . (19),$$

where B is a constant

This can be explained as follows. The solubility h generally decreases with the temperature according to a formula similar to (19). However, according to a similar law D increases more rapidly. The final result is that P increases with temperature. To show that the permeability is very different from case to case, we may refer to the figures of Table 24.

TABLE 24.
PERMEABILITY TO GAS OF SOME POLYMERS

Conditions	Peratimeon-coefficient in $\dfrac{cm^3.\ cm.}{cm^2.\ sec.\ atm.}$ 10^{-8}
Water vapour in cellulose triacetate	27000
Water vapour in natural rubber	1500
Water vapour in polystyrene	700
Water vapour in cellulose triacetate	11
Oxygen in cellulose triacetate	0.8

[1] K. WURSTLIN, *Kolloid-Z.*, 105 (1943) 9.

[2] See G. J. VAN AMERONGEN, *Thesis*, Delft 1943; R. M. BARRER, *Trans. Faraday Soc.*, 35 (1939) 628, 624; 36 (1940) 644.

[3] A. S. CARPENTER and D. F. TWISS, *Ind. Eng. Chem., Anal Ed.*, 12 (1940) 99.

[4] The number of cm^3 gas of 760 mm and 0° C, which are dissolved in 1 cm^3 of polymer at 1 Atm.

In the permeation by liquids, essentially the same principles are true as in the permeation by gases. A complication is, however, that above a relative humidity of 75 per cent HENRI's law is no longer valid. This means that the solubility increases more quickly than would be expected according to the law (see Fig. 50).
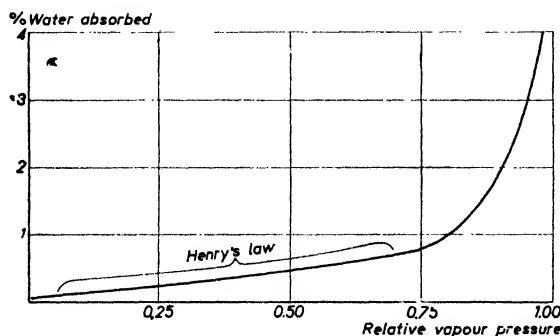
Fig. 50. Increase of the solubility of water with relative humidity.

For this reason, h in formula (18) will be much higher, leading to an increased permeation. Moreover it is to be expected that D in the saturated condition will be higher than in the unsaturated condition, leading to a still higher value for P. Little reliable scientific work is available here; we restrict ourselves to giving a picture in Fig. 51 concerning the diffusion constants for water in various materials.

The extent to which polymers are capable of absorbing water is of great importance in connection with the electrical properties. For practical tests, the absorption of liquids is mostly measured during a certain time and, for
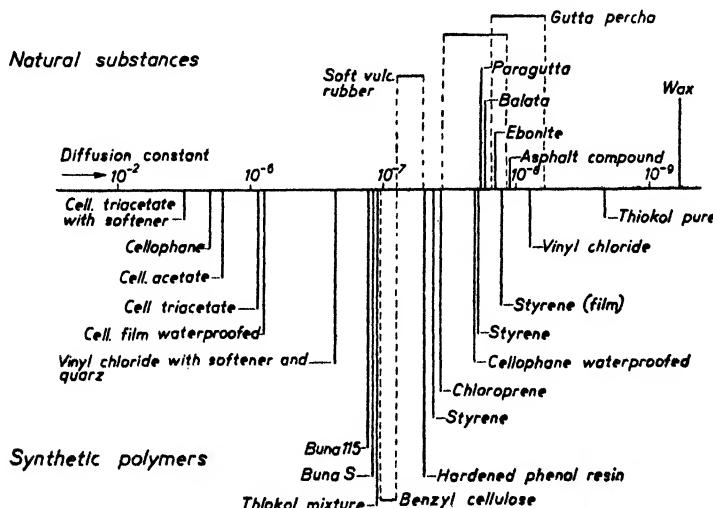
Fig. 51. Diffusion constants for water in natural and artificial materials. [1]

[1] W. M. H. SCHULZ, *Kunststoff-Techn. u. Kunststoff-Anwend.*, 10 (1940) 249.

instance, the amount absorbed in a week is taken as a basis for comparison. For scientific purposes, the diffusion constant is used.

§ 22. DETERMINATION OF MOLECULAR WEIGHT [1]

The molecular weight of polymers can be determined by chemical and physical methods, but on account of the polymolecularity both methods generally yield only average values. In order to obtain the molecular weight of the individual fractions, they should be separated. This is possible in scientific work but it is too complicated in industry and hence in the literature the average values are usually indicated.

a. Chemical methods.

When the constitution of the macro-molecule is known exactly and when characteristic groups are present — e.g., the terminal groups — then from the quantitative determination of these groups, conclusions may be drawn with regard to the degree of polymerization. If one final group is found per 1000 basemolecules then the degree of polymerization is 1000, etc.

A source of uncertainty connected with this method is that it is not easy to ascertain whether *all* macro-molecules bear the same terminal groups. As the length of the molecule increases the accuracy diminishes, because the percentage of characteristic groups then becomes smaller and smaller. In the case of certain high molecular acids good results have been obtained, as the COOH-final group can be easily titrated. In many other cases, however, the method has failed.

The conversion of certain macro-molecules into others (e.g., acids into esters) represents a chemical method which, as an aid to the physical methods to be discussed under b, can serve as a check. Thus, if the molecular weight ascertained for the high molecular acids is correct, then the same molecular weight should be found again for the corresponding esters. Hydrolytically degraded starch forms a prominent example in which this has been achieved. [2]

b. Physical methods.

Six methods for determining the molecular weight are available: 1, viscosimetrically; 2, by sedimentation (ultracentrifuge); 3, osmotically; 4, by diffusion; 5, with aid of the solubility (precipitability); 6, by measuring the scattering of light.

[1] H. MARK and P. M. DOTY, *The High Polymer Molecule, Its Weight and Weight Distribution*, New York.
[2] H. STAUDINGER and E. HUSEMANN, *Liebigs. Ann. Chem.*, **527** (1937) 195.

1. The *viscometric* [1] method has been developed in particular by the Stau-dinger school. On the basis of the Einstein formula (13) mentioned on p. 55, Staudinger has established the so-called viscosity law (20)

$$\frac{\eta_r - 1}{c} = K_m \, P \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (20)$$

in which η_r = relative viscosity (see p. 55), c = concentration, K_m = a constant which is characteristic for a certain polymer, and P = degree of poly-merization.

For every polymer the value of K_m should first be determined with the aid of low molecular representatives, the molecular size of which can be measured in the ordinary way. The molecular weight is then calculated on the basis of formula (20) from the $\dfrac{\eta_r}{c}$ values which are found. Against this extrapolation objections have been raised. It is true that the method receives support from the fact that after chemical modification the derivatives ob-tained from a macro-molecule showed the same molecular weight. This however is not necessarily a valid proof because if a mistake is made in the original extrapolation, why should the same error not repeat itself with the derivatives?

Staudinger [2] himself has checked the viscometric method by the appli-cation of other physical methods (see below) and has come to the conclusion that in certain cases — in which he supposes a branched molecule instead of a linear molecule — the viscometric method produces lower values for the molecular weight than, for instance, the osmotic method. Thus, for rubber he found a molecular weight five times higher.

At present most experimental results [3] point in the direction of a more general formula than that of Staudinger:

$$\frac{\eta_r - 1}{c} = KP^\alpha \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (21),$$

where α is a constant, varying between 0.6 and 0.9. For polyisobutylene 0.64 is found, for [4] GRS 0.66 and for polyesters 0.85. It thus appears that the Staudinger formula (20) is a special case (with α = 1) of the more general formula (21).

2. The *ultracentrifugal* [5] method is used on the sedimentation of the macro-

[1] See for a survey: E. O. Kraemer in R. E. Burk and O. Grummit, *The Chemistry of Large Molecules*, New York 1943, p. 78.
[2] H. Staudinger und Kl. Fischer, *J. prakt. Chem*, **157** (1941) 19, 158.
[3] R. Houwink, *J. prakt. Chem.*, **157** (1940) 15; P. J. Flory, *J. Am. Chem. Soc.*, **65** (1943) 372.
[4] D. M. French et al., *Rubber Chem. and Technol.*, **20** (1947) 984.
[5] See for a summary: T. Svedberg and K. O. Pedersen. *The Ultracentrifuge*, London 1940; E. O. Kraemer in, R. E. Burk and O. Grummit, *The Chemistry of Large Molecules*, New York 1943, page 95.

molecules in a powerful centrifugal field. From the sedimentation velocity measured, the molecular weight and, what is also of particular importance, the distribution of the molecular weights can be calculated. However, this excellent method requires such a complicated apparatus that it can only be applied in a few laboratories. ·

3. The *osmotic* [1] method is applicable to high molecular substances by using osmotic cells with semi-permeable membranes. The interpretation is based on the VAN 'T HOFF formula:

$$P = \frac{RT}{M} c \ldots \ldots \ldots \ldots \ldots (22)$$

in which P = osmotic pressure; c = concentration; R = gas constant; T = temperature. Taking into account certain factors according to MEYER [2] it is now possible to measure the molecular weight up to 400,000 with reliable results.

4. The determination of the *precipitability* has, on account of its simple character, a special attraction. When gradually adding a non-solvent to a high molecular solution, the precipitation of the largest molecules commences first and after a further addition the smaller ones follow. This is known to us already from equation (12) on page 54. SCHULZ [3] has rendered this method accessible for the determination of molecular weights by developing the formula

$$\chi = \delta + \frac{\beta}{P^m} \ldots \ldots \ldots \ldots \ldots (23)$$

in which χ = amount of precipitant; P = degree of polymerization; δ, β, m = constants.

5. The *scattering of light* is a new method [4] opening an independent way of determining the molecular weight of polymers.

Surveying the results obtained with the aid of all these methods, it should be said that we do not know accurately the molecular weight of the majority of polymers because the different methods often contradict each other. However, we are at the point at which at least the order of magnitude can be established, and in that we possess a standard of comparison for the different molecular weights in one and the same homologous series of polymers. For certain substances (proteins) we know the molecular weight with great exactness (work of SVEDBERG).

[1]　See for a summary: E. O. KRAEMER, *l. c.*
[2]　K. H. MEYER, *Natural and Synthetic High Polymers*, New York 1942.
[3]　G. V. SCHULZ, Z. physik Chem., **A 179** (1937) 312; **B 46** (1940) 105.
[4]　P. DEBYE, *J. Applied Phys.*, **15** (1944) 338.

CHAPTER IV

PROPERTIES; THEIR STANDARDIZATION AND TESTING[1]

§ 23. THE SITUATION IN DIFFERENT COUNTRIES

a. *General situation.* In different countries the methods of testing and the specifications thus derived have been developed independently. Mostly the data obtained are not real physical constants but arbitrary values dependent on the size of the test piece and the method applied. This rarely makes a comparison possible and for this reason the specifications in the most important countries will be discussed separately.

In all countries we find for *plastomers* seven chief groups of properties which are tested, namely: mechanical, thermal, electrical, optical, ageing, chemical and miscellaneous properties. The first three groups are in most cases sufficient for a first rough classification.

Of course, there ought to be international co-operation, but taking into account that the apparatus, test pieces and methods in use to measure a certain property are *often completely different in the various countries*, it will be clear that such co-operation is very difficult.

For *synthetic elastomers* the standardization was much easier because most existing testing methods for natural rubber could be applied without modification. The special properties of synthetic rubbers (oil resistance, etc.) made the development of some additional tests necessary, however. The same holds good for *fibres* and to a certain extent also for *lacquers*. It will appear that especially for lacquers [2] and artificial leather [3] it is not easy to express the physical properties in units. The cause of this is that the values found are closely connected with the properties of the underlayer.

For artificial leather special testing methods have been developed; these will not be discussed in detail [3].

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[1] The subject of this chapter is treated in full in R. Houwink, Elastomers and Plastomers, Amsterdam 1948, vol. 3.

[2] A complete review of the testing of films and fibres is given by A. V. Blom in R. Houwink, *Chemie und Technologie der Kunststoffe I*, Berlin 1942, p. 287.

[3] For instance see: W. M. Munzinger, *Kunstleder-Handbuch*, Berlin 1940, Ch. I; H. Herfeld and R. Schubert, *Kunststoffe*, 31 (1941) 169.

Usually the official specifications are expressed in minimum values. As these are often far below the values found in actual practice, we will mention average values in the Tables 25 and 26 (pg. 82-87).

b. In *U.S.A.* the American Society of Testing Materials, Philadelphia, closely co-operating with the National Bureau of Standards at Washington, is the leading organisation and in the A.S.T.M. Standards the most important methods of testing are well defined. Especially during the war, this work was much extended.

For *plastomers* the A.S.T.M. specifications [1] are now quite advanced. They do not confine themselves to the thermosetting materials as is usual in the other countries; official specifications for the thermoplastics are also given in great detail. The phenolic compounds are classified under 10 headings according to their properties, which are in this case practically dependent only on the kind of filler. Cellulose nitrate plastics are classified under 4, methacrylate plastics under 2 headings, etc.

Apart from these official specifications there exist now in the U.S.A. extensive tables [2], containing data for most properties of plastics.

For *rubbers* the testing methods are completely specified [3], but minimum requirements are expressed in units only for special purposes (electrical insulation, oil resistance).

For *fibres* the A.S.T.M. Standards are also very complete [4].

For *lacquers*, varnishes and paints extensive specifications are available [5].

c. *In Great Britain* the British Standards Institution, London, carries out the standardization [6]. Here, as in most other countries, the testing of the *thermosetting types* of plastics is much advanced. The reason for this may be that these are the older types for electrotechnical purposes and just here there was a need for specifications because cheap substitutes (asphalt mixtures) with a low heat resistance and strength spoiled the market. BSS 771 classifies thermosetting moulding materials and mouldings under five headings (see page 158).

For thermoplastics there exist some specifications, but these are far from complete, some materials being more or less covered [7], others not. In many

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[1]   A S T M Standards on Plastics, Soc. Test. Mat., Philadelphia 1945. See also Federal Specification L.P.-406a: Plastics, organic: General Specif., Test Methods, Superintendant of Documents, Washington D.C.

[2]   Technical Data on Plastics, Plastic Materials Manuf. Assoc., Washington, 1945; *Modern Plastics Encyclopedia*, New York 1947, Vol. I, page 729; A S T M Standards on Plastics, Philadelphia 1945; Very complete tables with data on elastomers and plastomers are found in R. Houwink, loc. cit. on pg. 70.

[3]   A S T M Standards on Rubber and Rubberlike Materials, Philadelphia 1945.

[4]   A S T M Standards on Textile Materials, Philadelphia 1944.

[5]   A S T M Standards on Paints, Lacquers and Varnishes, Philadelphia 1946.

[6]   B S S. 771 (Synthetic Resin Moulding Mat. and Mouldings). Further, B S S. 316, 474, 488, 547, 668, 972, 1137; Standard- Specif. on Paints, Lacquers and Varnishes. B S S. 2 D 50 Cellulose Acetate; B S S. F 56 Transparent sheets.

cases the Ministry of Aircraft Production has also issued specifications [1] under the reference DTD which takes into account special exigencies.

For rubbery materials most existing methods for testing rubber [2] could be applied without any modification. However, certain additional methods had to be developed.

d. *In Germany* the standardizing of *plastomers* before the war was in advance [3] of that in other countries. Here also the thermosetting materials were especially considered and the V D E (Verein Deutscher Elektrotechniker) has issued a complete book of specifications [4] concerning these materials.

As in the other countries the materials were classified in types according to some chief characteristics based on mechanical, thermal and electrical properties. Here especially the phenolic and urea types, acetylcellulose, asphalt and natural resin mixtures and some inorganic materials like lead borate and cement were covered. This has a historical background. The specifications were developed in order to distinguish the newer synthetics from the older asphalt and cement containing materials, in particular for electrical purposes.

The Germans have succeeded in making their specifications a lively contribution to the industry; this cannot always be said of other countries, where many people regard them as an unavoidable burden. For this purpose in Germany a system of industrial control was introduced. All factories of moulding materials were visited regularly by a representative of the M.P.B.D. (Material Prüfungsamt Berlin-Dahlem) and samples were taken from the running production. From these samples specimens were moulded and tested at the institute. Those factories in which the materials were regularly found to fulfil the requirements were allowed to press in their products the initials MPBD and a number referring to the factory involved. This was a guarantee of quality for buyers.

Apart from that, the Germans have tried to introduce a method for testing the moulded products in their final form in order to avoid the procedure of moulding separate test pieces. To this end they developed a testing machine (Dynstat = Dynamic-Static) on which the dynamic and the static properties of very tiny test pieces ($1.5 \times 4 \times 10$ mm) could be measured [4]. The dynamic test covered the impact strength, the static test the flexural strength. This method was not yet sufficiently reliable however to make it a basis for the official classification; moreover, micro-tests for the heat resistance and the electrical properties were still missing. In the author's opinion, however, it

[1] D T D. 315 Pigmented Cell. Acetate Sheets; D T D. 339a Methyl-methacrylate Plastics.
[2] Brit. Stand. Methods of Testing Vulcanized Rubber, Brit. Stand. Inst. 903, London 1940.
[3] Summaries are given by W. Zebrowski in R. Houwink, *Chemie und Technologie der Kunststoffe I*, Leipzig 1942, p. 278 and 325; P. O. Schupp, *ibid.*, 371; R. Nitsche und G. Pfestorf, *Prüfung und Bewertung elektrotechnischer Isolierstoffe*, Berlin 1940.
[4] V D E Vorschriftenbuch, Berlin 1939.

will be a point of paramount importance to work out these ideas in more detail because the only things that matter for the consumer are the properties of the final product he gets in hand.

The testing of *elastomers* was also at a high level [1] in Germany and it was stimulated especially by the pre-war development of synthetic rubbers in that country. The same can be said about the testing of *fibres* [2] and *lacquers* [3].

e. *Other countries.* In *Switzerland* a special system of classification has been developed [4] in which the thermosetting materials are denoted by H (Härtbar) and the thermoplastics by T (Thermoplast). However various special test methods [5] based on similar principles as in the other countries are used. We shall not consider this system further because in our opinion — considering the abundance of systems already existing — it is wrong that a small country should develop a new system of its own.

In *France* [6] a system was adopted of the same type as the German system. Here also a quality mark exists which is controlled on the basis of official specifications.

In *Holland* tentative specifications have been developed [7] similar to the German system.

§ 24. TESTING[8]

Although the testing methods are often very different in the various countries, it will appear that the basic principles are in many cases the same. For this reason stress will be laid on these principles only. We will as a rule discuss only those methods the results of which can be expressed in units so that we can use them in this book for the purpose of making comparisons. Less important methods will be neglected.

a. Viscous properties.

1. *Solubility.* For the control of the polymerization or condensation processes the *solubility test* is important, especially in the first stage of the reaction.

[1] Cf. for a summary: S. RESSINGER in J. D'ANS, *Chem. techn. Untersuchungsmethoden.* Ergänzüngswerk zur 8. Aufl. III, Berlin 1940, p. 395.

[2] H. SOMMER und H. MANDRZYK in J. D'ANS, *loc. cit.*, p. 197, and W. WELTZIEN and K. WINDEK-SCHULZE, *ibid.*, p. 264.

[3] W. TOELDTKE in J. D'ANS, *loc. cit.*, p. 470.

[4] *Bull. Schweiz. Elektr. Ver.*, **18** (1936) 531.

[5] V S M Normblatt (Zürich) 77101, 77102, 77103, 77104, 77105, 77106, 77107, 77108, 77111, 77112, 77113.

[6] Union Technique des Syndicats de l'Electricité (U S E), Paris. Nos. 1008, 1009, 1010, 1011, 1012.

[7] Normaalblad V 918, V 1508, V 1509, V 1510, V 1511, V 1512, (The Hague, 1944 and 145).

[8] J. H. Teeple in R. Houwink, *loc. cit.* on pg. 70.

In linear polymers, the solubility decreases as the chain length increases, according to the considerations on page 54.

For three-dimensional polymers it can be said that, as long as the material is still completely soluble no particles of $< 10^4$ Å diameter have formed.

2. *Viscosity.* In the early stages of the production process many plastomers and elastomers exist in a viscous state. The viscosity can be determined with the aid of a series of more or less classical apparatus. [1] In most of these the time of flow through a capillary is measured.

3. *Plastometry.* If the viscosity is higher, say $> 10^5$ poises, the flowing process becomes too slow, and then the application of pressure is necessary, leading to the use of plastometers. [2] The three chief types in use are pictured in Fig. 52.

a. Parallel plates.   b. Extrusion.   c. Rotary.
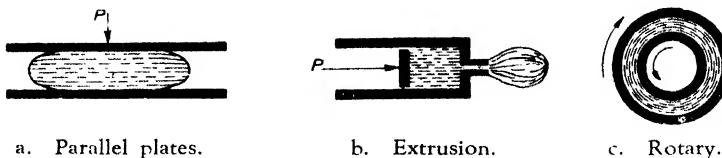
Fig. 52. Main types of plastometers.

For thermosetting materials the rotary type (MOONEY plastometer [3]) cannot be used since the instrument cannot be cleaned quickly. For these the extrusion type is most popular and the ROSSI-PEAKES flow tester is a good example.[4] In England and the U.S.A. the cup flow test has been standardized [5]; it stands between the parallel plate and the extrusion type.

4. *Creep and cold flow* are properties of paramount importance in heavy constructions. Although testing methods exist,[6] the official specifications are still unsufficiently developed.

b. Mechanical properties.

1. *Tensile strength, modulus of elasticity, elongation at break and permanent set.* [7] These properties should be physical constants independent of the test-piece and method of testing. This is not the case, however, but a rough

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[1] A summary is given by R. N. J. SAAL. in *Second Report on Viscosity*, Roy. Acad. Sci., Amsterdam 1938.

[2] For a summary see C. J. VAN NIEUWENBURG in *Second Report on Viscosity*, Roy. Acad. Sci., Amsterdam 1938.

[3] M. MOONEY and R. H. EWART. *Physics.*, 5 (1934) 350.

[4] A S T M D 569-43.

[5] B S S. 771-1938.

[6] A S T M D 674—42 T; D 530—44 T; D. WARBURON BROWN, *Handbook of Engineering Plastics*, London 1945, p. 86; R. BURNS and J. L. HOPKINS, *Modern Plastics*, 14 (1937) 42

[7] A S T M D 638-42 T; D 651-42 T; B S S 903/1940; B S S 771/1938; D I N/D V M 3504.

comparison is usually possible if the speeds of testing and the cross-sections of the test-pieces are of the same order of magnitude. Test-specimens (Fig. 53) usually consist of a bar with a reduced section in the centre (dumbbell).
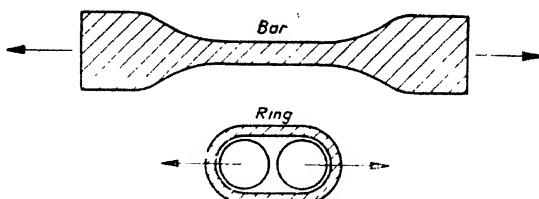
Fig. 53. Principles of the tensile test.

For rubbers, rings are also used. However, they give notably lower values.

Most machines are constructed in such a way as to continuously record stress and strain; see Fig. 26 pg. 31 for the stress-strain curves of some representative materials. When the initial part of the curve obtained is a straight line through the origin, its inclination is a measure of the *modulus of elasticity*. For technical purposes the stress is usually calculated for the original cross section. For scientific purposes it is preferable to calculate it for the actual area during the test, which can make the final results for rubbers more than ten times higher. In the case of brittle materials, extremely accurate testing machines are required in order to avoid local stress concentrations. The *permanent set* can be easily determined by measuring the length of the test piece after release of the stress within a certain arbitrary time.

In the lacquer and synthetic leather industry it is more usual to apply technological instead of purely physical methods for measuring the elasticity of films. Lacquered metal is, for instance, bent in some conventional apparatus and the degree of bending at which the film begins to shear is decisive. The ERICHSEN test [1] is a sample of this type.

2. *The flexural strength*, often referred to as bending strength [2], is the maximum bending load sustained by the specimen and converted to maximum fibre stress. Essentially it measures the same as the tensile strength, and for rigid materials the values are roughly two times those found for the tensile strength. The principle is illustrated in Fig. 54.

On page 72 we mentioned that in Germany a micromethod (Dynstat) has been developed.

[1] See A. V. BLOM, Paint, Oil Chem. Rev., 101 (1939) No. 5.
[2] A S T M D 790-44 T; D 650-42 T; V D E 0302.

3. *Impact strength or shock resistance.* For practical purposes, where objects are exposed to dynamic influences (shocks), the impact resistance (see page 38) is much more important than the tensile strength. On page 39 it was already
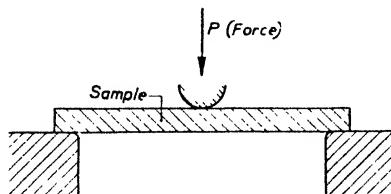
Fig. 54. Principle of the bending test.

pointed out that this property essentially measures the toughness, i.e. the energy required for breaking the specimen in a dynamic test. It has also been shown, however, that the practical results deviate widely from theoretical expectations. The consequence is that if impact tests are carried out in different ways, the results obtained vary to a large extent so that no correlation exists between the individual methods. As pointed out on page 39 the test is made with notched and with plain bars; the difference is very striking. For practical purposes the first method is far more important and for this reason it is comprehensible that in some countries the method with plain bars is not officially prescribed. The two principles for supporting the test rod are pictured in Fig. 55. The Germans have also introduced here their micro-method (Dynstat), but it appeared very difficult to obtain reliable results on small test pieces for materials with coarse fillers.

a. Simple beam   b. Cantilever beam
(Charpy type) [1]   (Izod type) [1]
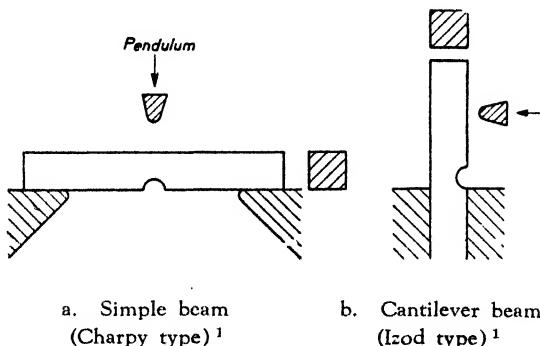
Fig. 55. Principles for carrying out the impact test.

A S T M. D 256-43 T; B S S 903.

4. *Hardness.* The hardness is usually determined by pressing a steel ball into the material being tested and by measuring the diameter of the permanent impression after removal of the load. According to the type of material, loads between 10 and 100 kg (22 to 220 lbs) are applied; the diameter of the steel balls varies from 2.5 to 12.5 mm. It is deplorable that even for such an extremely simple method no unity of specifications exists. In Europe the BRINELL method is very popular; in U.S.A. the ROCKWELL test is more often applied. [1] These methods are not suited to thin materials (varnish layers), because then the properties of the underlayer influence the results. This influence is felt more strongly for softer materials. For a hard type of rubber a thickness of 4 mm is sufficient to be independent of the underlayer, for soft types, a thickness of 12 mm is required [2]. In such cases the hardness can be measured by means of a scratch test [3] or with the aid of a swinging pendulum [4] which is placed on the lacquered surface; damping occurs sooner for softer films.

For measuring the hardness of rubbers the impression of the steel ball must be measured without removal of the load [5], because otherwise the recovery would influence the result. For most thermoplastics the same holds good.

Essentially, the modulus of elasticity also measures the hardness, andfor scientific purposes this method is to be preferred.

5. *The compressive strength* is the maximum compressive load sustained by the specimen divided by the original cross section (Fig. 56).
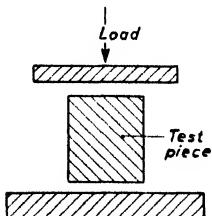
Fig. 56 Principle of testing the compressive strength.

6. *The tear resistance* is not yet very popular for the testing of plastics. For rubbers it is of more importance. It is determined by means of [6] the so-called crescent tear test shown in Fig. 57. The test piece is stretched and the force necessary for tearing at the nick is recorded.
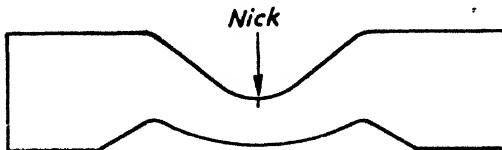
Fig. 57. Testing the tear resistance of rubbers.

[1] A S T M. D 785-44 T.
[2] J. R. SCOTT, *J. of Rubber Research.* 26 (1948) 9. Here also a comparison between various instruments for measuring the hardness is given.
[3] See e.g., H. NIESEN, *Farben-Z.* , 45 (1940) 804.
[4] G. G. SWARD, *Circ. Nat. Paint, Varnish, Lacquer Assn.*, Washington, 410 (1936); 510 (1936).
[5] A S T M. D 676-44 T; B S S.-903.
[6] A S T M. D 624-44.

7. *Fatigue tests* are of great importance and are well specified for rubbers[1] and for plastics [2], but generally they are not yet sufficiently developed to be written into official specifications. Usually they are carried out by bending a test piece frequently and noting the number of cycles necessary for break.

c.   Thermal properties.

1. The *softening point* or *distortion under heat* for fusible resins and easily flowing plastics can be determined by measuring the temperature at which they show a certain extent of flow without any application of external pressure (drop point). When the material is so highly viscous that it would only flow sufficiently if heated above its decomposition temperature, pressure is applied in order to force it to flow [3]. For very hard, highly polymerized materials heavier forces are neccessary [4]. This can be realized by applying long bars according to one of the principles of Fig. 58. Usually the temperature is raised gradually and that temperature at which a certain degree of deflection is observed is called the softening point.
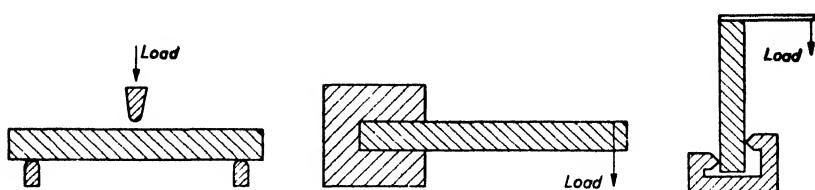
a.   American test [5]   b.   British test [6]   c.   German test [7]

Fig. 58. Principles for determining the softening point of plastics.

2. *The continuous resistance to heat* measures a chemical instead of a physical property. It is the temperature at which the material can be kept continuously without being chemically decomposed (cracked). It is usually specified by the temperature at which a certain loss of weight can be observed in a period of a few days. For many purposes, e.g., in cases where the material is carried by a layer of another material (lacquers), this specification is more practical than the softening point.

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[1] A S T M. D 623-41 T.
[2] A S T M. D 671-42 T; D. WARBURON BROWN, *Handbook of Engineering Plastics*, London 1945, p. 72; VDI Forschungsheft 1939, page 396.
[3] The penetration method (A S T M. D 5-25) and the Ring and Ball method (A S T M. D 36-25) are examples rhereof.
[4] In the VICAT test a needle is forced into the material under a 5 kg load.
[5] A S T M. D 648-45 T.
[6] B S S 771 and 903.
[7] V D E 0302 (MARTENS test).

3. *The inflammability* is tested [1] by pressing a test-specimen against a surface at bright red heat (950° C = 1640° F). The burning rate is expressed in cm or in inches per minute. The Germans denoted this test [2] as ,,Glutfestigkeits-prüfung''.

d. Electrical properties.

1. *The electrical resistance* is found in a conventional way [3] by measuring the current which flows through the specimen when placing it between two electrodes.

2. *The surface resistance* is found [3] by placing two parallel electrodes on a flat surface and measuring the current which flows over the moist surface.

3. *The dielectric strength* is measured [4] by placing the specimen between two electrodes and increasing the electric tension at a uniform rate until breakdown occurs.

4. *The arc resistance* is measured [5] by the time required for rendering the surface conductive owing to carbonization by an arc formed between two electrodes.

5. *Power factor and dielectric constant (permitivity)* are the physical constants describing the behaviour of an insulator in the alternating field. Tests are carried out [6] on flat specimens by means of a SCHERING bridge.

In many cases the materials are conditioned in a moist atmosphere or by immersion in water before the electrical tests are carried out. The reason for this is that, in practice, insulation materials are often used under wet conditions and because their unfavourable properties only then come into being (formation of ions).

e. Permanence properties; ageing tests.

There are numerous accelerated ageing tests in which the samples are submitted [7] to cycles of high and low temperatures, to high and low relative humidities, to infra-red and ultra-violet light. None of these is entirely satisfactory because in practice circumstances are always different. They give, however, approximate indications about the future behaviour when in use. For rubbers some tests have been standardized, leading to a general interpre-

[1] A S T M. D 757-44 T.
[2] V D E 0305.
[3] A S T M. D 257-38; B S S. 771 and 903.
[4] A S T M. D 149-44; B S S. 903.
[5] A S T M. D 495-42.
[6] A S T M. D 150-42 T; B S S. 903.
[7] A S T M. D 756-44T, D 795-44T.

tation all over the world. In the GEER-EVANS test[1] samples are kept in air at 70°C (158° F) for one week, which is said to correspond to 3 to 5 years in practice. In the BIERER-DAVIS test, the specimens are exposed to oxygen at 20 atm. and 70° C (158° F). The mechanical properties are determined before and after the test; their degree of alteration is an expression of the ageing properties.

f. Water absorption.

The water absorption is measured in various countries with the aid of test pieces of different dimensions. This excludes a comparison between the results obtained, so that here also there is an urgent need for international co-operation, which could come about very easily.

g. Permeability.

The permeability of films to volatile liquids can be measured[2] according to the principle of Fig. 59.

The film is placed between two jars, one filled with the liquid; the gain of weight of the empty jar is measured. In a very similar way the permeability to gases can be determined. Reference may be made to the fact that often in the literature the coefficient of permeation is erroneously called the diffusion coefficient. The two coefficients differ from each other by the factor h (solubility), see page 65.

h. Chemical resistance.

The chemical resistance is tested by immersing specimens in the testing liquid for say 7 days at 25°C (77° F). The changes in weight, dimensions and appearance are observed. For a general orientation a long list of chemicals can be investigated[3], but for special purposes the special chemicals involved should be examined experimentally.
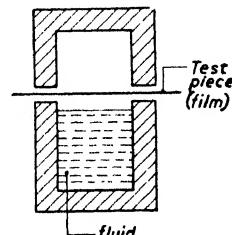
Fig. 59. Principle of measuring permeability.

§ 25. CHEMICAL ANALYSIS

When pure polymers are to be identified, this is practically always possible by means of a systematic chemical analysis[4]. The identification of mixtures

[1] A S T M. 428-36T; D I N. D V M 3508.
[2] A S T M. D 814-44T; D 697-42T.
[3] A S T M. D 543-43T.
[4] The complete analysis is described by G. F. D'ALELIO, A Laboratory Manual, etc., New York 1943, p. 111, and by A. G. EPPRECHT in R. HOUWINK, Elastomers and Plastomers, Amsterdam 1948, Vol. 3; T. G. P. SHAW, Ind. Eng. Chem., Anal. Ed., 16 (1944) 541; H. MARK and T. RATH, High Polymer Reactions, New York 1941.

is often very difficult and requires great skill. In many cases, when polymers of a very similar constitution are present, very ingenious and complicated apparatus is necessary. The mass spectrometer [1] for the analysis of mixtures of synthetic rubbers is a striking example. There are, however, mixtures which cannot be analyzed.

In practice, often only a rough identification of the type of polymer involved is wanted [2]. Then a comparison with the behaviour of known samples when heated slowly, or when decomposed by dry distillation or on burning in an open flame often leads to a result. The fact as to whether or not the material becomes plastic on heating makes it possible to discriminate between the thermoplastic and the thermosetting types. The odours on burning in a flame easily betray the presence of materials like phenols, urea, etc. The behaviour on being dissolved and the fluorescence on exposure to ultra-violet light can give valuable additional information.

A separate problem is the identification of fillers. When they are of inorganic nature, the polymer is decomposed by heating and the filler can be identified along the usual lines of classical analytical chemistry. When the fillers are of an organic nature, methods for removing the polymer by extraction must be followed. These are different from case to case.

§ 26. TABULATION OF PROPERTIES

In Table 25 a survey [3] of the most important properties of plastomers is given; in Table 26 the same has been done [4] for elastomers.

No attempt has been made to give a complete survey [5] of all properties, but only those which are characteristic and of practical importance have been considered.

The figures mentioned usually express *mean* values as encountered in the general literature.   •

[1] Research Paper, Bur. of Standards, Washington, R.P. 1664.
[2] A description is found in A. G. Epprecht. loc. cit. on page 80.
[3] Compiled by J. W. F. VAN 'T WOUT, Rubber Foundation, Delft.
[4] Compiled by B. B. S. T. BOONSTRA, Rubber Foundation, Delft.
[5] See: R. HOUWINK, *Elastomers and Plastomers*, Amsterdam 1948. Vol. 3.

TABLE 25. PROPERTIES

No.	Plastomer	Filler	Particulars	Specific gravity	Tensile strength ASTM D 638	
					kg/cm^2	psi
	Phenolics					
1	Phenol-formaldehyde	none	cast	1.31	560	8000
2	Phenol-formaldehyde	wood-flour	moulded	1.4	560	8000
3	Phenol-formaldehyde	ground slate	moulded	1.8	480	6000
4	Phenol-formaldehyde	asbestos	moulded	1.8	480	6000
5	Phenol-formaldehyde	paper cuttings	moulded	1.35	350	5000
6	Phenol-formaldehyde	fabric cuttings	moulded	1.4	560	7000
7	Phenol-formaldehyde	pulp preformed	moulded	1.4	640	8000
8	Phenol-formaldehyde	paper base	laminated	1.33	840	12000
9	Phenol-formaldehyde	cotton fabric	laminated	1.33	700	10000
10	Phenol-formaldehyde	glass fabric	laminated	1.6	1020	16000
11	Phenol-formaldehyde	wood veneer	laminated	1.3	2200	32000
12	Aniline-formaldehyde	none	moulded	1.23	630	9000
13	Aniline-formaldehyde	paper base	laminated	1.21	700	10000
	Carbamides					
14	Urea-formaldehyde	α-cellulose	moulded	1.5	500	7000
15	Melamine-formaldehyde	α-cellulose	moulded	1.5	500	7000
16	Melamine-formaldehyde	asbestos	moulded	1.8	420	6000
17	Melamine-formaldehyde	glass fabric	laminated	1.9	1500	21000
	Vinyl derivatives					
18	Ethylene	none	—	0.92	140	2000
19	Styrene	none	—	1.06	420	6000
20	Dichlorostyrene	none	—	1.38	400	6000
21	Vinyl chloride-acetate	none	rigid	1.35	420	6000
22	Vinylidene chloride	none	moulded	1.68	390	5500
23	Vinyl alcohol	none	—	1.25	270	3000
24	Vinyl butyral	none	rigid	1.1	420	6000
25	Methyl methacrylate	none	formed	1.19	560	8000
26	Allyl ester	none	cast	1.32	390 ·	5500
	Cellulose derivatives					
27	Cellulose acetate	—	moulded	1.35	350	5000
28	Cellulose acetate-butyrate	—	moulded	1.2	280	4000
29	Cellulose nitrate	camphor	formed	1.4	450	6500
30	Ethyl, cellulose	—	moulded	1.15	420	6000
31	Vulcanized fibre	—	sheeted	1.3	560	8000
	Proteins					
32	Casein-formaldehyde	—	formed	1.34	700	10000
33	Super-polyamide (nylon)	none	moulded	1.15	700	10000
34	Super-polyamide (nylon)	none	fibre	1.1	3500	50000
	Rubber derivatives					
35	Chlorinated rubber	none	moulded	1.64	280	4000
36	Hydrochlorinated rubber	—	film	1.16	250	3500
37	Cyclized rubber	none	—	1.06	280	4000
	For comparison					
38	Steel	—	—	7.8	12500	180000
39	Cast iron	—	—	7.2	1500	21500
40	Oak wood (length)	—	—	0.8	900	13000
41	Hard rubber	none	moulded	1.15	700	10000

	Mechanical Properties				Thermal Properties					
		Impact strength			Heat distortion point				Inflamma-bility	
Modulus of elasticity		IZOD notched ASTM D 256	VDE		ASTM D 648		Continuous resistance to heat		1 = non-inflamma-ble. 5 = in flammable	
			un-not-ched	not-ched						
10^4 kg/cm², 10^5 psi		ft lb/in	cm kg/cm²		°C	°F	°C	°F		
										No.
3	4	0.3—0.5	5	1.2	40—80	110—180	215	420	3	1
8	12	0.3—0.5	7	1.8	138	280	130	265	2	2
12	17	0.6	5	1.7	150	300	215	420	1	3
17	24	0.3—1	6	2.5	150	300	215	420	1	4
8	12	—	10	7.1	135	275	130	265	2	5
8	11	1—8	15	14	135	275	120	250	3	6
8	11	3	—	—	—	—	120	250	3	7
3—21	4—30	5	30	24	>160	>320	110	230	2—3	8
3—11	4—15	5	50	25	>160	>320	110	230	3	9
11	15	25	—	—	>160	>320	215	420	1	10
25	37	6	92	91	>160	>320	110	230	3	11
3.5	5	0.32	15	2	110	230	—	—	3	12
5	7	—	23	—	100	210	—	—	2	13
8	12	0.4	7	1.5	132	270	82	180	2	14
7	10	0.4	7	1.7	195	380	130	265	2	15
11	16	0.35	—	—	195	380	130	265	1	16
—	—	—	—	—	195	380	130	265	1	17
0.1	0.15	no break	—	—	50	120	100	212	4	18
3	4	0.45	250	5	75	170	70	160	4	19
3—5	4—7	1—1.5	—	—	114	236	—	—	3	20
3	4	0.4	—	—	63	145	55	130	1	21
1.5	2	0.3—1	—	—	74	165	82	180	1	22
—	—	—	—	—	—	—	—	—	4	23
3	4	1.0	150	—	52	125	50	122	4	24
3	4	0.4	20	—	88	190	70	160	4	25
2	3	0.35	—	—	70	160	100	212	—	26
1.5	2	1—6	25	15	70	160	82	180	4	27
1.5	2	1—9	—	—	60	140	82	180	4	28
2	3	4.5	150	12	63	145	60	140	5	29
2	3	3—11	—	—	70	160	82	180	4	30
5	7	4—8	100	17	—	—	177	350	3	31
4	6	1.0	30	1.7	150	300	155	310	3	32
2	3	0.5—1	>140	12	77	170	—	—	4	33
2—4	3—6	—	—	—	—	—	—	—	4	34
1.5—4	2—6	0.1—3	10	—	60	140	—	—	1	35
—	—	—	—	—	—	—	—	—	—	36
3.5	5	2.6	—	—	88	190	—	—	4	37
200	290	—	—	—	—	—	—	—	1	38
200	290	—	12	—	—	—	—	—	1	39
10	14	—	30	—	—	—	—	—	4	40
3	4	0.5	15	—	—	—	—	—	4	41

TABLE 25. (CONTINUED)

	Plastomer	Filler	Manufacturing	Electrical Properties		
				Specific resistance	Dielectric constant at 10^6 cycles	Power factor $\times$ 10^3 at 10^6 cycles
				ohm cm		
No.	**Phenolics**					
1	Phenol-formaldehyde	none	cast	10^{12}	7.4	75
2	Phenol-formaldehyde	wood-flour	moulded	10^{11}	5—10	45
3	Phenol-formaldehyde	ground slate	moulded	10^{12}	5—8	60
4	Phenol-formaldehyde	asbestos	moulded	10^{10}	7	60
5	Phenol-formaldehyde	paper cuttings	moulded	10^{11}	5	45
6	Phenol-formaldehyde	fabric cuttings	moulded	10^{10}	5	45
7	Phenol-formaldehyde	pulp preformed	moulded	—	—	—
8	Phenol-formaldehyde	paper base	laminated	10^{11}	5—10	50
9	Phenol-formaldehyde	cotton fabric	laminated	10^{11}	5—10	50
10	Phenol-formaldehyde	glass fabric	laminated	—	4.5	25
11	Phenol-formaldehyde	wood veneer	laminated	—	5—10	50
12	Aniline-formaldehyde	none	moulded	10^{16}	3.5	7
13	Aniline-formaldehyde	paper base	laminated	—	5	40
	Carbamides					
14	Urea-formaldehyde	α-cellulose	moulded	10^{12}	7	35
15	Melamine-formaldehyde	α-cellulose	moulded	10^{12}	7	40
16	Melamine-formaldehyde	asbestos	moulded	10^{11}	7	40
17	Melamine-formaldehyde	glass fabric	laminated	—	7	10
	Vinyl derivatives					
18	Ethylene	none	—	$> 10^{17}$	2.3	0.4
19	Styrene	none	—	10^{18}	2.5	0.2
20	Dichlorostyrene	none	—	—	2.6	0.2
21	Vinyl chloride-acetate	none	rigid	$> 10^{14}$	3.0	14
22	Vinylidene chloride	none	moulded	10^{15}	4	40
23	Vinyl alcohol	none	—	10^{7}	—	—
24	Vinyl butyral	none	rigid	$> 10^{14}$	3.3	7
25	Methyl methacrylate	none	formed	$> 10^{15}$	3.1	25
26	Allyl ester	cast	cast	—	3.6	60
	Cellulose derivatives					
27	Cellulose acetate	—	moulded	10^{11}	4.5	50
28	Cellulose acetate-butyrate	—	moulded	10^{11}	5	25
29	Cellulose nitrate	camphor	formed	10^{11}	6	85
30	Ethyl-cellulose	—	moulded	10^{12}	3	27
31	Vulcanized fibre	—	sheeted	10^{6}	7	40
	Proteins					
32	Casein-formaldehyde	—	formed	—	6.5	52
33	Super-polyamide (nylon)	none	moulded	10^{12}	3.7	55
34	Super-polyamide (nylon)	none	fibre	—	—	—
	Rubber derivatives					
35	Chlorinated rubber	none	moulded	10^{18}	3	6
36	Hydrochlorinated rubber	none	film	—	—	—
37	Cyclized rubber	none	—	10^{16}	2.7	2
	For comparison					
38	Steel	—	—	50.10^{-6}	—	—
39	Cast iron	—	—	—	—	—
40	Oak wood (length)	—	—	—	5	—
41	Hard rubber	none	moulded	10^{16}	3	7

	Chemical Resistance						
Water absorption ASTM D 570 (in 24 h.)	Acids		Alkalis		Alcohol	Gasoline Animal and Vegetable oils	
	weak	strong	weak	strong			
%	r — resistant		m — medium			d — dissolves	No.
0.5	r	m	m	d	r	r	1
0.7	r	m	m	d	r	r	2
0.1	r	m	m	d	r	r	3
0.3	r	m	m	d	r	r	4
0.7	r	m	m	d	r	r	5
1	r	m	m	d	r	r	6
0.7	r	m	m	d	r	r	7
1—9	r	m	m	d	r	r	8
1—9	r	m	m	d	r	r	9
1.5	r	m	m	d	r	r	10
3—11	r	d	m	d	r	r	11
0.1	m	d	r	m	r	r	12
0.1	m	d	m	m	r	r	13
1.5	r	d	m	d	r	r	14
0.4	r	d	m	d	r	r	15
0.1	r	d	m	d	r	r	16
2	r	d	m	d	r	r	17
0.01	r	r	r	r	r	m	18
0.05	r	r	r	r	r	m	19
0.03	r	r	r	r	r	m	20
0.2	r	r	r	r	r	m	21
0.1	r	r	r	r	r	r	22
>100	m	d	r	m	d	r	23
2	m	d	r	d	d	r	24
0.5	r	m	r	m	m	r	25
0.2	r	m	r	r	r	r	26
4	m	d	m	d	d	r	27
2	m	d	m	d	d	r	28
2	m	d	m	d	d	r	29
2	m	d	r	r	d	r	30
18—70	m	d	m	d	r	r	31
7—14	m	d	m	d	r	r	32
1.5	m	d	m	d	r	r	33
5.5	m	d	m	d	r	r	34
0.2	r	r	r	m	r	r	35
—	r	m	r	m	r	d	36
0.02	r	r	r	r	r	m	37
—	d	d	r	d	r	r	38
—	d	d	r	d	r	r	39
45	r	d	r	d	r	r	40
0.02	r	m	r	r	r	m	41

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TABLE 26. PROPERTIES

No.	ELASTOMER	FILLER (volume on rubber)	MANUFACTURING	Spec. grav.	Tensile kg/cm² (ASTM)
1	Natural rubber [1]	none	crude	0.91	30
2	Natural rubber [1]	none	vulc.	0.96	310
3	Natural rubber [1]	ca. 25% carb. bl.	vulc.	1.12	310
4	Natural rubber [1]	ca. 25% carb. bl.	vulc. with tetramethyl-thiuram disulphide (tuads)	1.12	310
5	Butadiene-styrene copolymer [2] (G R S)	ca. 30% carb. bl.	vulc.	1.12	210
6	Butadiene-styrene copolymer [1] (Buna-S)	ca. 30% carb. bl.	vulc.	1.15	225
7	Butadiene-acrylic nitrile [1] (G R A)	ca. 30% carb. bl.	vulc.	1.2	290
8	Chloroprene polymer [1] (Neoprene G)	none	vulc.	1.32	300
9	Chloroprene polymer [1] (Neoprene G)	20% carb. bl.	vulc.	1.4	275
10	Isobutylene [3]	none	not vulc.	0.91	40
11	Isobutylene-isoprene (Butyl) [4]	30% carb. bl.	vulc.	—	200
12	Polyvinyl chloride (Koroseal)	50% plasticizer	---	1.3	170
13	Ethylene polysulphide [1] (Thiokol B)	35% carb. bl.	vulc.	1.65	45
14	Silicone [5]	none	vulc.	2	35

TABLE 26 (CONTINUED) PROPERTIES

No.	ELASTOMER	FILLER (volume as % of rubber)	MANUFACTURING
1	Natural rubber [1]	none	crude
2	Natural rubber [1]	none	vulc.
3	Natural rubber [1]	ca. 25% carb. bl.	vulc.
4	Natural rubber [1]	ca. 25% carb. bl.	vulc. with tetramethyl-thiuram disulphide (tuads)
5	Butadiene-styrene copolymer [2] (G R S)	ca. 30% carb. bl.	vulc.
6	Butadiene-styrene copolymer [1] (Buna-S)	ca. 30% carb. bl.	vulc.
7	Butadiene-acrylic nitrile [1] (G R A)	ca. 30% carb. bl.	vulc.
8	Chloroprene polymer [1] (Neoprene G)	none	vulc.
9	Chloroprene polymer [1] (Neoprene G)	20% carb. bl.	vulc.
10	Isobutylene [3]	none	not vulc.
11	Isobutylene-isoprene (Butyl) [4]	30% carb. bl.	vulc.
12	Polyvinyl chloride (Koroseal)	50% plasticizer	—
13	Ethylene polysulphide [1] (Thiokol B)	35% carb. bl.	vulc.
14	Silicone [5]	none	vulc.

[1] R. HOUWINK, Elastomers and Plastomers, Amsterdam 1948, Vol 3.
[2] Rubber Age, 54, (1943) 247; MACNEAL, ibid, 53 (1943) 31; VILA, Ind. Eng. Chem., 34, (1942) 1269.
[3] TH. LIGHBOWN et. al., Ind. Eng. Chem., 32 (1940) 1283; Rubber Age, 51 (1942) 377.
[4] H. BARRON, Modern Synthetic Rubbers, London 1947, p. 261.
[5] Dow-Corning pamphlet.
[6] Some data is borrowed from A. J. WILDSCHUT, Technol. and Physical Investigations on Natural and Synthetic Rubbers, Elsevier New York 1946; Plastics Catalog, New York 1946.
[7] A S T M: D 624—44 Crescent; lb/in thickn. Nat. rub. = 640 (for comparison).
[8] lb per 0.1 in thickness.
[9] Goodyear flex testingmachine; G. R. VILA, loc. cit.

Mechanical Properties [6] | Ageing Properties

strength	Elong. at break	Tear resist.[10]		Perm. set [11]	Dynam. fatigue [12]	Hardness	Modulus at 300%		Maximum service temperature		Geer-Evans test 70°C. (158°F.) in air.	Bierer-Davis test in O_2 at 20 atm.	
p. s. i. (BSS)	%	kg/cm²	p. s. i.	%	10³x	Shore A Duro-meter	kg/cm²	p. s. i.	°C	°F	Weeks for 25% decrease in tensile strength	% decrease in tensile strength after 1 week at 70 °C (158 °F).	No.
430	1000	—	—	100	—	25	8	115	—	—	—	—	1
4400	750	90	1300	4	700	45	18	260	—	—	8	12	2
4400	600	200	2900	10	140	65	70	1000	150	300	8	—	3
4400	600	200	2900	10	1000	60	65	950	150	300	25	8	4
3000	580	—	400 [7]	—	21 [9]	60	83	1190	150	300	4	8	5
3200	550	55	800	10	1500	68	75	1050	150	300	15	12	6
4100	600	55	800	10	1000	60	50	700	150	300	20	5	7
4300	950	55	800	10	>2400	40	20	290	160	320	26	12	8
3900	750	180	2600	6	>2400	65	60	850	160	320	20	18	9
600	600	15	10 [8]	—	—	35	7	100	150	300	> 8	0	10
2800	700	—	40 [8]	6	1500	55	32	450	150	300	25	0	11
2400	325	120	1700	35	1500	70	150	2190	—	—	> 8	7	12
650	250	40	570	45 (at 75 % elong.)	0.8	75	45 (at 200 % elong.)	650	95	200	> 8	5	13
330	200	—	—	—	—	70	—	—	300	570	—	0	14

Electrical Properties | Chemical Resistance

Spec. resistance	Diel. const. (800 cycles)	Tg δ (800 cycles)	Diel. Strength	Water absorption	Acids		Alkalis		Al-co-hol	Pet-rol; oils	Ben-zene	Ke-tones; Esters	No.
					strong	weak	strong	weak					
Meg-ohm. cm		10.⁴	KV/mm	In % after 1 week immersion at 20°C. (2 mm thickness)	r = resistant; m = medium-resistant; d = dissolves, swells or decomposes								
10⁹	2.4	25	15	5	m	m	m	m	m	d	d	m	1
10⁹	3	60	25	1.4	m	m	m	r	m	d	d	m	2
—	—	—	—	0.9	m	m	m	r	m	d	d	m	3
10⁸,¹⁷	4.5	30	25	1.0	m	m	m	r	m	d	d	m	4
10²	4.5 [19]	100 [19]	—	—	m	m	m	r	m	d	d	m	5
10⁸,¹⁷	3	—	20	0.4	m	m	r	r	m	d	d	m	6
—	11	450 [13]	—	0.8	m	m	m	m	m	r	d	d	7
10⁸	7.5	300 [18]	23	2	m	m	m	m	r	r	d	m [11]	8
—	—	—	—	1	m	m	m	m	r	r	d	m	9
10¹⁰	2.1	4	25	3 [15]	r	r	r	r	r	d	m	r	10
3	2.1	4	20	2.4 [15]	r	r	r	r	r	d	m	r	11
10⁶	8	1500[14]	20[14]	0.5 [16]	r	r	r	r	r	m	d	d	12
—	—	—	—	0.4	m	m	d	d	m	r	m	m	13
10	7.5	13	20	1.7	m	m	m	r	r	m	d	r	14

[10] Tensile strength of a testpiece with incisions.
[11] % elongation remaining 1 hr after release from 200% extension for 24 h.
[12] Number of cycles after which flexcracking becomes visible with a pocket lens.
[13] Insulation mixture with 40% rubber.
[14] With 50% plasticizer.
[15] At 100° C. Comparative for nat. rubber = 12.
[16] After 24 hrs.
[17] Without carbon black.
[18] For Neoprene E.
[19] 60 Cycles.

CHAPTER V

PROCESSING OF POLYMERS

The process of manufacturing a finished article from the polymer is often a long one. The methods used in this connection will be treated shortly in this chapter.

§ 27. MIXING AND KNEADING

The manufacturing of mixtures is simplest when the polymer itself is a liquid or when, with the aid of a liquid, a solution (e.g., a lacquer) has to be manufactured. Simple stirring machines or mixers, of which Fig. 164 (p. 214) is an example, are used.

The equipment must be of heavier construction when the liquid is more viscous and especially when pigments have to be dispersed in it, because then
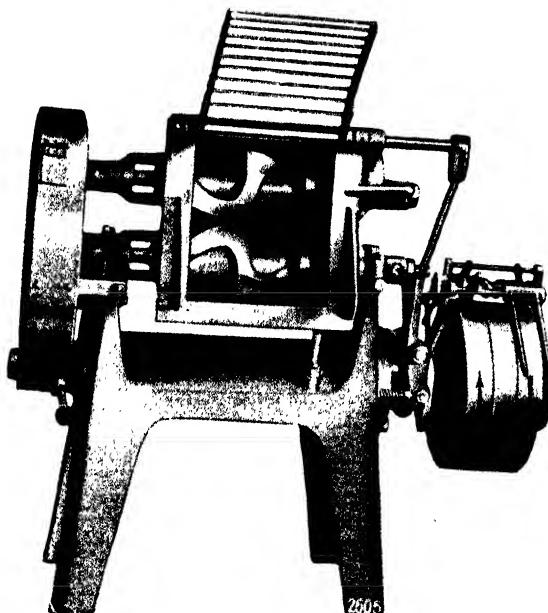
Fig. 60. Simple kneader, tilted for emptying
(construction BAKER PERKINS).

a strong grinding action is required of the machines. In cases where dispersion of pigments is not necessary, a kneader as in Fig. 60 is used (e.g., for the mixing of syrup-like resins with cellulose flakes). The dispersion and grinding of pigments requires a totally different machine (like the one shown in Fig. 61) in which for the manufacturing of pastes the material is ground continually between two rollers placed close together. Moreover, it is pulverized between the lower roller and a bar which can be pressed against it. There are also machines in which this bar is pressed against the roller by means of hydraulic pressure. The grinding and dispersion of pigment particles [1] is an extremely important point in the paint and rubber industries, due to the necessity for the extreme fineness of some pigments. Often varnish films are about 20 μ thick and in such cases the grinding of the pigments has to be carried out at least until the particles are of this degree of fineness. Ball mills also find a large-scale application for such purposes; mills up to 1000 gallons capacity are used at present in the manufacture of paints.

←— pressure bar

←. scraper
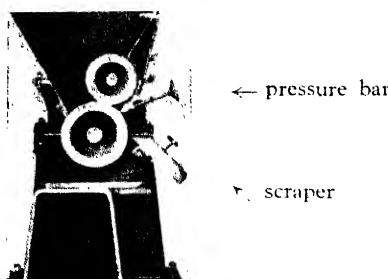
Fig. 61. Roller for grinding and mixing paints.

If the material is very hard or tough and does not have to be dissolved, e.g., if rubber is mixed with compounding ingredients, the mixing can be done by first plasticizing the polymer by heating, which is best carried out by masticating the material on hot rolls. The viscosity is mostly still very high and therefore heavily constructed machines are needed. We find heavy kneaders, built as in Fig. 60, or machines having two rollers with a differential rotation rate, represented in Fig. 62. This picture shows the two important phases during such a mixing process in the case of rubber. In Fig. 62a the high molecular product is still tough and not yet capable of incorporating the compounding ingredients; in Fig. 62b the pasty condition is reached in which fillers can readily be incorporated. The possibility of mixing is limited by the capability of the machines in working up the material. If it is impossible to render the material sufficiently plastic by masticating and

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[1] See for this subject: J. J. MATTIELLO, *Protective and Decorative Coatings*, New York 1944.

heating, this may be achieved sometimes by adding solvents or softeners. If for some reason or other this cannot be effected, then the manufacturing of such mixtures is scarcely possible. Of course, there are cases in which no high demands are made regarding the dispersion of the powders added and then the dry substances can be ground in a ballmill (see Fig. 135 page 179). This method is frequently applied for adding dyes to moulding powders.
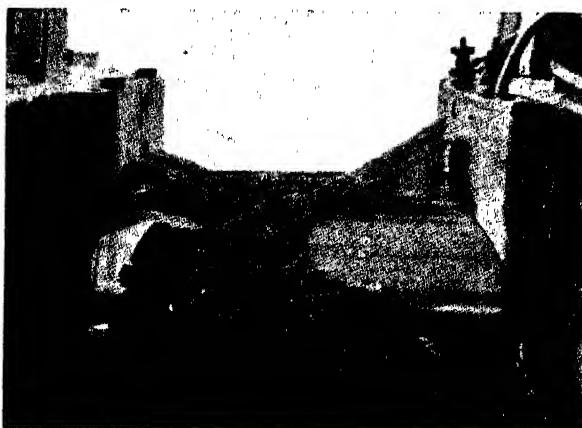
a. The beginning of the process. The material is still tough and elastic.
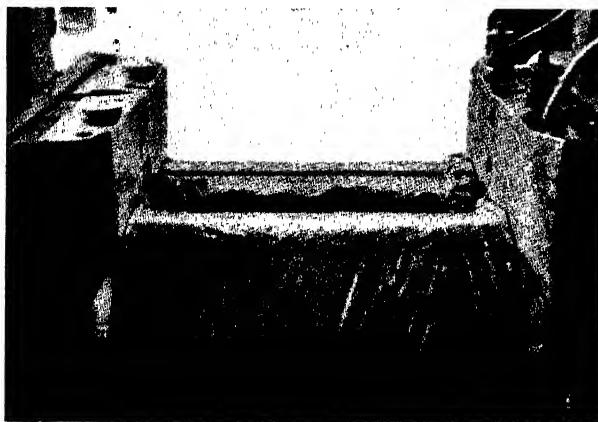
b. The end of the process. The compounding ingredients can now be added.

Fig. 62. Plasticizing of rubber.

§ 28. MOULDING, EXTRUDING, LACQUERING, ETC.

The methods for further processing are naturally also closely connected

with the consistency of the material. An attempt is always made to work up
the materials in as thinly-liquid a state as possible, because then more lightly
constructed apparatus suffices.

a. Liquid state.

The liquid state is utilized for casting, lacquering, dipping, spreading and
spinning. These processes are schematically represented in Fig. 63.
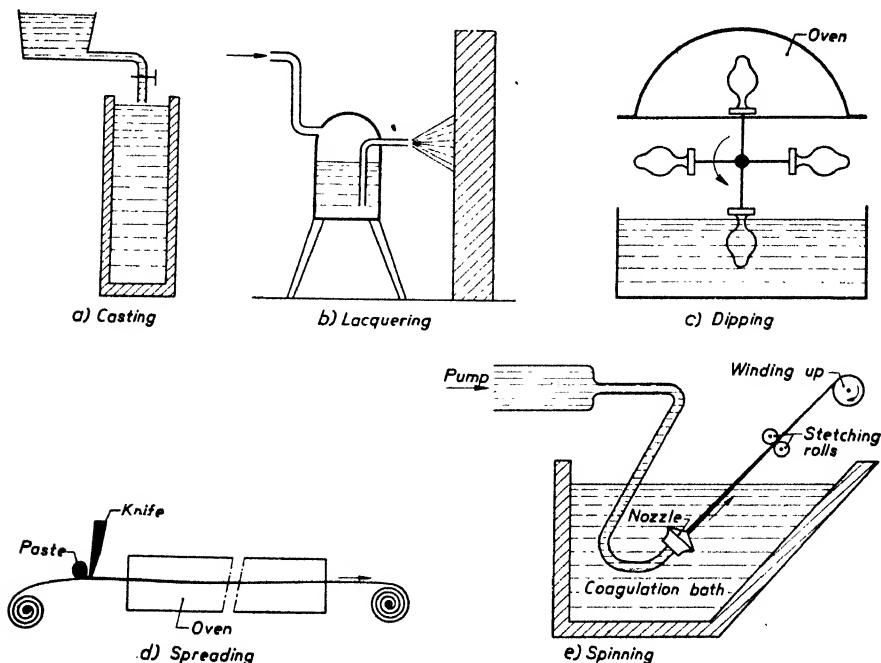
Fig. 63. Processing in the liquid state.

The *casting* (Fig. 63a) is especially simple, but nevertheless is little employed
in the industry of plastics because the majority of polymers are not obtain-
able [1] with a sufficiently low viscosity. In Fig. 121 (page 168) we shall encounter
some articles which have been manufactured by pouring the liquid phenol
resin into glass or nickel moulds. The latter are then gradually hardened by
heating them slowly. Many articles can be made from such castings on the
lathe or by some other mechanical operation.

For *lacquering* (Fig. 63b), the brush or the spray pistol is used.

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[1] It might be started from the monomers but bulk polymerization would then have
to be applied.

For *dipping* (Fig. 63c), a mould is brought into the solution; after its removal a thin layer adheres which is then dried. This operation can be repeated as often as necessary in order to obtain the desired wall thickness. Rotatory machines have been built for this purpose.

The *spreading* method (Fig. 63d) is similar to the calendering which is to be discussed below; the mass is used as a paste and is spread with a knife on a roll of paper or fabric and then dried in an oven. Artificial leather, for example, is manufactured by such a process.

For *spinning* (Fig. 63e), a thick solution is pressed through a nozzle and the extruded thread is either precipitated in a coagulating bath (viscose silk) or dried in an oven (acetate silk). On p. 199 we shall consider the details of these methods. A variation of this method is the casting of films, in which a flat slit is used instead of a round nozzle. One can also pour the solution onto a roller, allow it to coagulate and then strip off the film, thus arriving at a kind of drum casting method.

b. Plastic state.

The plastic state is at least as important for forming purposes as the thinly-liquid state, because for the majority of polymers the latter state cannot be realized by the application of heat, in consequence of the too high molecular structure of the material.

The *calendering* shown in Fig. 64a is done by rolling the pasty plastic mass into a sheet between two rollers; the sheet is then pressed by a third roller on a base of fabric. As against spreading, calendering offers the advantage that no solvent is needed. When it is necessary to bring the plastic *between* the threads of fabric, the *frictioning* process is applied. The rolls then have a different speed and much more pressure is required.

The *extruding* of endless rods or tubes is represented schematically in Fig. 64b. This method, which consists in forcing the material through a nozzle with the aid of a plunger or a worm, originates from the rubber industry, but with insignificant modifications it can be applied to many synthetic materials as well (see page 157). In practice, Fig. 65 represents the extruding of a large hollow tube. Technique is now so far developed that thermosetting compounds also can be extruded in a continuous process. It has proved possible to apply [1] this extrusion method to the filling of moulds; a set of moulds rotates in order to facilitate a quick alternation of the filling, the curing and

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[1] *Plastics Catalog*, New York 1945, p. 499.

a) Calendering

b) Extruding of tubes, rods, etc

c) Drawing

d) Blowing of hollow articles from sheets

e) Blowing of hollow articles

f) Compression moulding

g) Pressing of laminates

h) Low pressure moulding

i) Injection moulding and jet moulding

k) Transfer moulding
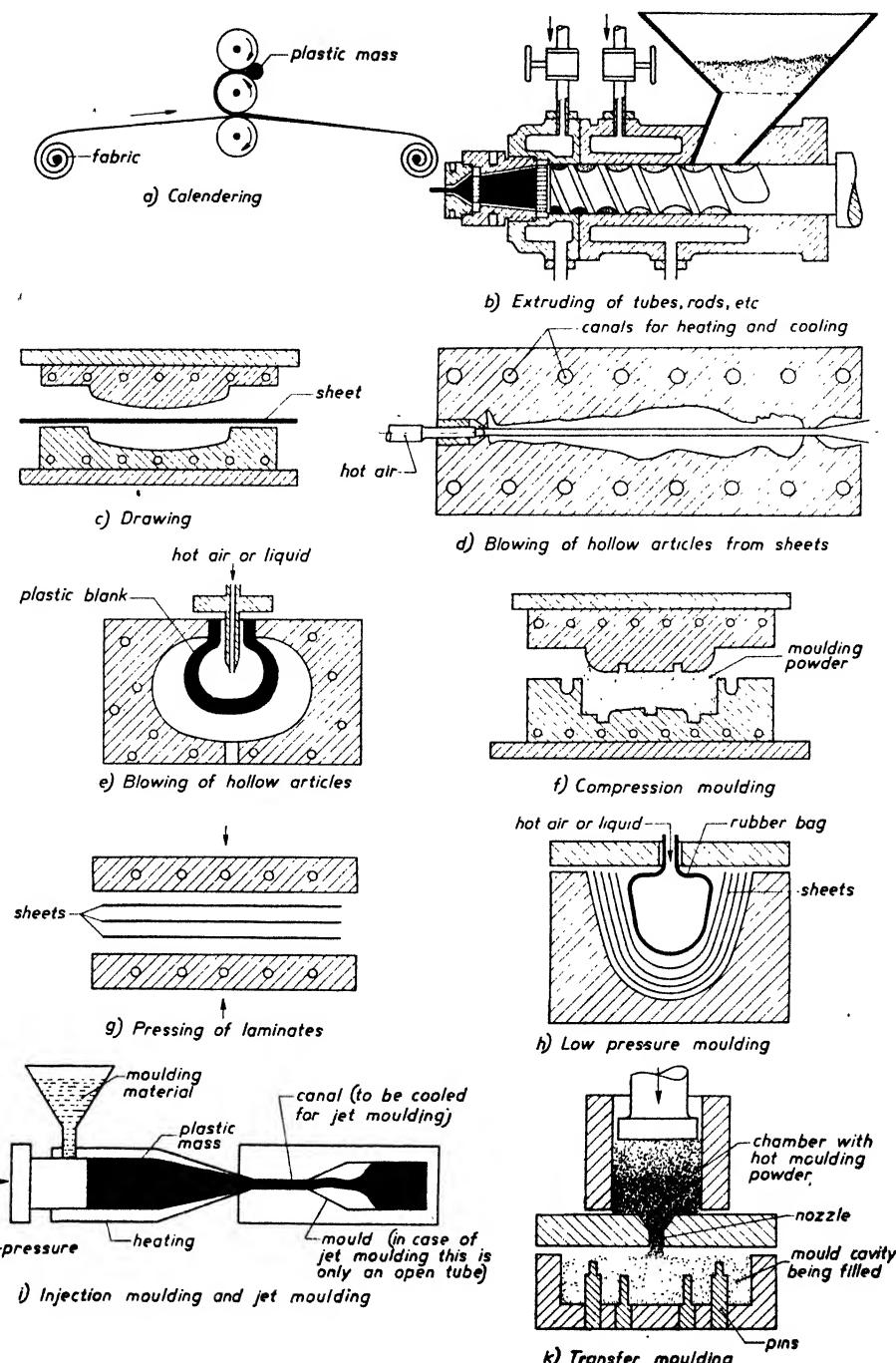
Fig. 64.   Processing in the plastic state.

the discharge operations. Extruders are also used at present for feeding calenders, leading to a simple continuous method for making films.

Fig. 65. Extruding of a hollow tube.

The *drawing* (swaging) of articles from a sheet (Fig. 64c) can be effected with any thermoplastic material under the application of heat. Nowadays, even deep drawing is possible; a bell jar 0.002 in thick has been drawn to a depth of 50 cm (18 inches).

The *blowing*, according to Fig. 64d, is a very similar process; it is an old technique in the manufacturing of hollow celluloid articles. Air is blown between two hot parallel sheets of the polymer. Consequently these sheets are forced against the walls of the mould and so form a hollow object. No flow in the direction of the sheets can take place, making it impossible to manufacture articles with a non-homogeneous wall strength.

The *blowing of hollow articles* starting from a blank is one of the latest refinements in plastics industry [1]. It can be carried out according to the principle shown in Fig. 64e. First a blank is formed with the aid of an auxiliary removable mould and this is blown into a bottle under air or fluid pressure (see page 111). In contrast to blowing, starting from sheets, flow of the material can take place here in all directions so that an uneven wall thickness can result.

Compression moulding is one of the most popular techniques in the plastics industry; it is applied to the thermosetting materials in particular.

Plastics Catalog, New York 1945, page 487.

The steps of the moulding process are represented in Fig. 66.

As can be seen, the mould has a certain amount of idle room for taking up the loose voluminous powder; especially important is the possibility of pressing-in metallic parts N, based on the fact that the moulded piece shrinks more than the metal, keeping it firmly enclosed. It is important that, for compounds, the mould needs not be cooled; the softening point of the material becomes so high that at the moulding temperature of 150° C (302° F) the

a. Filled   b. Moulded   c. Final product
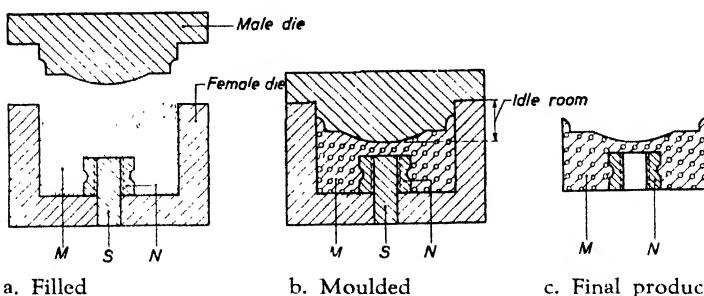
Fig. 66. Process for moulding the product M with pressed-in nut N; S = stift; m = moulding compound.

article is still hard. This contrasts with the thermoplastic substances which are very soft and not rigid at that temperature so that the mould has to be cooled. On page 181 a hydraulic press is shown. The pressure applied is usually of the order of 300 kg/cm² (4000 p s i), the temperature is 145 °C (294 °F).

To-day, besides the hydraulic presses, automatic rotary presses (Fig. 109) are also used which, in fact, are nothing more than tablet presses, shown in Fig. 68 (page 98), being very strongly built, however, and furnished with a heating arrangement. Such machines are attended by one man who brings the material into the mould, which is closed and opened automatically during a rotation, the moulded piece being ejected automatically. This rotary automaton is now competing with hydraulic presses with multiple moulds.

Lately a special method was developed for polyvinyl chloride, which is difficult to mould. The substance, while warm, is extruded into a vertical press, where it is pressed into cold moulds by a sudden blow.

Most mould constructions [1] can be traced back to a few basic principles and these are shown in Fig. 67.

They are identified by the type of seal between the plunger and cavity. On this basis one can distinguish between the flash type and the positive type; the semipositive mould is a compromise.

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[1] A detailed description of some moulds for mass production is found in *Plastics Monograph No. 24*, Instit. Plast. Ind., London 1945. See for tolerances: *Standard for tolerance on moulded plastic parts*. Soc. Plast. Inst., New York 1946; *British Plastics*, 14 (1943) 683. For mould designing see: J. H. DUBOIS and W. I. PRIBBLE. *Plastics Mold Design*, Chicago 1947. G. B. THAYER, *Plastics Molds*, Chicago 1946.

In the flash type, also known as the "overflow" mould, the upper and lower portions can rest one on top of the other. There must be a slight excess of moulding powder which is squeezed out at the joining point as the edges of
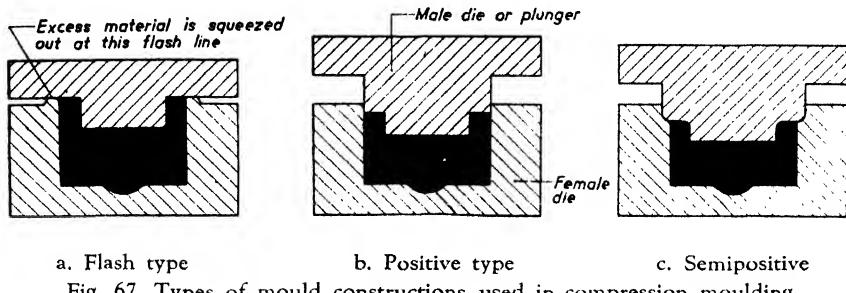
a. Flash type   b. Positive type   c. Semipositive
Fig. 67. Types of mould constructions used in compression moulding.

the mould come together; this is the flash. In the positive type the plunger is telescoped by the lower mould. The amount of intake of moulding powder is decisive for determining the thickness of the finished article because no material can escape. This type is less popular than the flash mould and is only used for deep drawn articles, since there is a better guarantee that all parts will be under sufficient pressure.

The pressing of *laminated* materials (Fig. 64g) is a very simple operation. During the war the technique of *low pressure moulding*, in which the laminates are compressed by means of gas or fluid pressure, was developed; the principle of this is shown in Fig. 64h. For an extensive description see page 166.

For thermoplastics, especially the *injection moulding* (see Fig. 64i) has gained special importance because the operation can be carried out solely with the use of automatic machines (Fig. 74, page 110). The heated plastic material is forced discontinuously through a nozzle into a water-cooled mould and cooled off quickly. During the period of cooling, the piston runs to the left so that a new flow of material out of the storage tank can take place. Then the piston runs again to the right and the period of moulding recommences. The output amounts to about 250 injections per hour, which is considerably higher than for compression moulding operations, where 15 per hour is a reasonable average. When we further consider that for small articles, as, for instance, tube closings, 12-fold moulds are used, then we arrive at an hourly output of 3000 pieces. Since one man is able to run such a machine, it is clear that the share of the wages in the finished piece is practically negligible and that the cost of the material plays the decisive part. Lately, machines have been built with a capacity of 600 g (22 oz) per injection. These will find increasing application because certain polymers like polystyrene are now becoming available at an equal volume price as phenolic moulding powders (see Chap. XVI).

The principle of injection moulding has also been applied to thermosetting materials, leading to the jet moulding and to the transfer moulding processes.

Jet moulding is a process [1] in which a thermosetting material is extruded under such an adjustment of the temperatures in the equipment that it first becomes plastic, in which stage an endless profile is formed. This is then continuously extruded and thus hardened. See for details Fig. 110.

Transfer moulding [2] can be carried out in an ordinary hydraulic press. The material is heated to the plastic condition in a separate chamber or outside the mould by means of high frequency electric current. From this chamber (Fig. 64k) it is transferred or injected into the mould cavity through runners. When the mould is completely filled, it is heated for a sufficient period to bring about the final polymerization.

The advantage of transfer moulding is, that the final pressure in the mould is not reached before it is completely filled. At that moment the pressure is evenly divided all over the mould wall and so partially unbalanced high pressures are avoided. Therefore these methods are applied particularly when intricate pieces with delicate inserts, requiring moulds with thin fragile projecting sections or long, slender core pins, have to be produced. Thanks to the fact that the mould is closed before the material enters the cavity, no flash is formed and so a high degree of precision can be obtained. The disadvantage is that the method is rather complicated. For this reason transfer moulding should be applied only when absolutely necessary.

c. Auxiliary equipment.

In many moulding operations it is necessary to preform the material into a *tablet*. This leads to a reduction of volume because the powder contains a lot of air which escapes during the tabletting operation. For a wood flour filled compound this compression ratio or bulk reduction is 1.8; for a rag filled compound it amounts to 6. This offers advantages because now the idle room of the mould (Fig. 66) can be considerably smaller. Moreover, tabletting machines automatically produce pills of a certain desired weight so that the problem of weighing is solved in a very simple manner. For quick mass production it is very convenient to make ball preforms which can be automatically loaded into the cavities of a multiple mould with the aid of some specially constructed auxiliary equipment. Fig. 68 shows such a tabletting machine in operation; it works entirely automatically and can be so easily controlled that one man can attend several machines, delivering thousands of tablets hourly. The pressure in such machines is very high and amounts to 1600 kg/cm² (10 tons per sq. inch).

[1] U.S. Pat. 2,296,295 and 2,296,296.
[2] For a description see: *Plastics Catalog*, New York 1945, p. 476.

In all these technical processes the *method of heating* is of great importance. Some 20 years ago steam was used almost exclusively; in older plants gas heating could be encountered here and there. After that, heating systems using hot
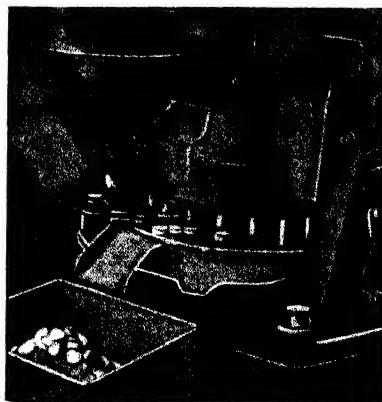
Fig. 68. Tablet press in operation.

water or hot oil under pressure were developed, but in later years electrical heating has become more and more popular. Large plants are still generally operated by steam as the general system; for special purposes, however, electric heaters are used in addition, especially where high or quickly changeable temperatures are wanted.

In recent years two new systems have been developed. Infra-red lamps are applied for surface heating, e.g., for stoving lacquers or for drying impregnated fabrics. High frequency heating, on the contrary, is used for large objects. The polymer is placed between electrodes in an alternating field and heat is developed in the material owing to dipole rotation (see page 63 for the causes of dielectric losses). Consequently the method cannot be applied to materials with a low tg δ, like polystyrene, polyethene and polyisobutylene. However, for a polar material like phenol-formaldehyde moulding powder the curing time of 7 min can be reduced to 2 min for an object with a wall of 10 mm (0.4 inch) thickness.

§ 29. MACHINING AND FINISHING

The majority of moulded products must be finished before shipment; this can be done by fraizing, sawing, drilling, tapping, grinding, sanding, etc. Flashes are mostly removed by tumbling, fins by hand filing. The finish is improved by tumbling or by buffing. In many cases, some printing, stamping

or marking operation is necessary. There exists a great difference between the various plastics regarding their ability to be finished; instructions are available [1].

As a general rule it may be taken for granted that three-dimensionally hardened materials (phenolics, ureas), on account of their brittleness, are difficult to machine. However, conditions can be improved by adding fine organic filling materials like wood flour. On the contrary, when adding inorganic substances like ground slate or asbestos, conditions become worse. Laminated materials on a phenol basis can be easily machined. In general, the thermoplastics are very easily worked; the rate of cutting should not be so great that much heat is produced causing the material to soften. Rubber-like substances offer more difficulties in finishing, especially when a great accuracy is required; in such cases they can be frozen in liquid air.

D. WARBURTON BROWN, Handb. of Engineering Plastics, London 1945; p. 168, Kunststoffe, 32 (1942) 143; Plastics Catalog, New York 1945; The Manipulation of Sheets, Rods and Tubes, Plastics Monograph 18, Inst. of Plast. Ind., London 1946

POLYMERS BASED ON ETHYLENE AND ITS DERIVATIVES [1]

In this chapter two groups are considered. First, the derivatives based on ethylene or vinyl ($CH_2 = CH_2$), and secondly, those based on methylethylene: $CH_2 = CH$. To the former belong ethylene, styrene, vinylcarbazole, $\underset{CH_3}{|}$ acrylic acids and their derivatives and vinyl ethers. To the latter belong isobutylene and methacrylic acid and its derivatives.

The ethylene polymers are all built up by chain-molecules and therefore are real thermoplastics.

§ 30. RAW MATERIALS [2]

Ethylene itself is obtained either during the cracking of petroleum at about 700° C (1300° F) or by dehydration of ethyl alcohol or ethyl ether with the aid of a catalyst (Al_2O_3) at 375° C (705° F).

For producing the monomers, special manufacturing processes have been worked out, the most important of which are summarized in Table 27. Here the monomers have been enclosed in frames and we shall see in the next paragraph how the polymers are obtained from them. Each synthesis of a monomer represents a method discovered by laborious research and one which is often in competition with other slightly different processes.

TABLE 27.
MANUFACTURING PROCESSES FOR THE MONOMERS

1. a. *Acetylene* + acetic acid ———→
$CH≡CH$

vinyl acetate
$CH_2=CH$
|
$OOCCH_3$

A. In the presence of Hg at 70° C (158° F), vinyl acetate is formed temporarily and is then quickly removed from the reaction mixture.

saponific.

vinyl acetate ———→

vinyl alcohol
$CH_2=CH$
|
OH

B. The gaseous reaction mixture is quickly conducted at 200° C (392° F) over Zn and Cd acetate which have been precipitated on finely divided carbon.

vinyl alcohol + $C_3H_7C\begin{smallmatrix}H\\\\O\end{smallmatrix}$ →

butyraldehyde

vinylbutyral
$—CH_2=CH---CH_2--- CH—$
$O \quad O$
$HC—C_3H_7$

[1] See H. GIBELLO, *Résines Viniliques*, Paris 1947.
[2] A complete description of the technology is given by H. T. NEHER, in R. HOUWINK, *Elastomers and Plastomers*, Amsterdam 1949, Vol. 2.

b. *Acetylene* + HCN ⟶

> acrylonitrile
> $CH_2=CH$
> |
> CN

c. *Acetylene* + hydrochloric acid →

> vinyl chloride
> $CH_2=CH$
> |
> Cl

The gaseous reaction mixture is conducted at 160° C (320° F) over mercury chloride precipitated on carriers.

vinyl chloride + Cl_2 → Trichloro-ethane $CH_2Cl—CHCl_2$ $\xrightarrow[\text{halogenation}]{\text{dehydro-}}$

> vinylidene chloride
> $CH_2=CCl_2$

d. *Acetylene* + alcohol ⟶

> vinyl ether
> $CH_2=CH$
> |
> OCH_3

The reaction is carried out at 170° C (338° F) under 15 - 20 atm in the presence of KOH in methanol.

e. *Acetylene* + carbazole ⟶

> vinyl carbazole
> $CH_2=CH$
> |
> N

The carbazole is added in the presence of strongly alkaline substances (KOH) by heating at 180° C (356° F).

2. a. *Ethylene* $\xrightarrow{\text{polymerization}}$ polyethylene at 1000 atm and 200° C
$CH_2=CH_2$

b. *Ethylene* + Cl_2 ⟶ ethylene dichloride $CH_2Cl—CH_2Cl$ $\xrightarrow[\text{halogenation}]{\text{dehydro-}}$

> vinyl chloride
> $CH_2=CHCl$

c. *Ethylene* + benzene $\xrightarrow[\text{90° C (194° F)}]{AlCl_3}$

> styrene
> $CH_2=CH$
> |
> C_6H_5

Next ethyl benzene is formed, which is converted into styrene by catalytic dehydrogenation at 600° C (1110° F).

d. Ethylene oxide + HCN ⟶ ethylene cyanohydrin $\xrightarrow{-H_2O}$

$CH_2—CH_2$ $CH_2—CH_2$
$\diagdown O \diagup$ | |
                 OH CN

> acrylonitrile
> $CH_2=CH$
> |
> CN

→

$\xrightarrow{\text{saponification}}$

> acrylic acid
> $CH_2=CH$
> |
> $COOH$

$\xrightarrow{\text{esterification}}$

> acrylic acid methyl ester
> $CH_2=CH$
> $C \diagup\!\!\!\diagup O$
> $\diagdown OCH_3$

3. *Acetone* $+$ HCN $\rightarrow$ acetone cyanohydrin $\xrightarrow[\text{and dehydro-genation}]{\text{saponification}}$

CH$_3$—CO—CH$_3$

$$CH_3—C\underset{CH_3}{\overset{OH}{\underset{\shortmid}{\overset{\shortmid}{-}}}}CN$$

methacrylic acid
CH$_2$=C—CH$_3$
$|$
COOH $\rightarrow$

$\xrightarrow{\text{esterification}}$

methacrylic acid methyl ester
CH$_2$=C—CH$_3$
$|$
C$\overset{O}{\underset{OCH_3}{\diagup}}$

4a.   *Petroleum* $\xrightarrow{\text{cracking process}}$

Isobutylene
$$CH_2=C\underset{CH_3}{\overset{CH_3}{\diagdown}}$$

b. CO$_2$ $+$ H$_2$ $\xrightarrow[\text{methanol synth.}]{\text{by-products of}}$ Isobutyl alcohol $\xrightarrow{-H_2O}$

HO—CH$_2$—CH$\underset{CH_3}{\overset{CH_3}{\diagup}}$

5a, *Propylene* $\xrightarrow[\substack{600° C \\ (1110° F)}]{Cl_2 \text{ at}}$ allyl chloride $\xrightarrow{\text{steam}}$ allyl alcohol

CH$_3$—CH=CH$_2$ CH$_2$Cl—CH=CH$_2$ CH$_2$OH—CH—CH$_2$ $\rightarrow$

allyl esters, e.g.
CH—CH$_2$
$|$
CH$_2$OOCCH$_3$
allyl acetate

b. (propylene) $\xrightarrow{O_2}$ propylene oxide

CH$_3$—CH—CH$_2$
$\diagdown$O$\diagup$ $\xrightarrow[300° C \ (572° \ F)]{Al \ at}$

c. (propylene) $\xrightarrow{H_2O}$ isopropanol $\xrightarrow{}$ acetone (See also 3).

It will be clear that in such an abundant field of chemical possibilities, new processes frequently come to the fore. Thus we may point to the discoveries of REPPE[1] for the inexpensive preparation of acrylic derivatives directly from acetylene. A compound with a labile hydrogen atom and acetylene is treated with CO in the presence of metal compounds, capable of forming carbonyls:

$C_2H_2 + CO + H_2O$ $\rightarrow CH_2 = CH — COOH$ Acrylic acid

$C_2H_2 + CO + ROH$ $\rightarrow CH_2 = CH — COOR$ Acrylic ester

$C_2H_2 + CO + RSH$ $\rightarrow CH_2 = CH — COSR$ Acrylic thioester

$C_2H_2 + CO + RNH_2$ $\rightarrow CH_2 = CH — CONHR$ N-substituted acrylic amide
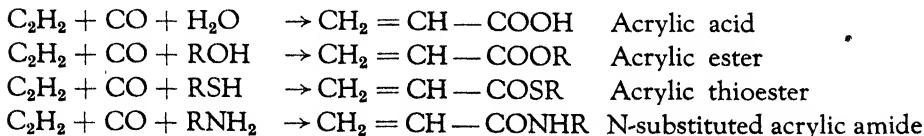
§ 31.   FORMATION OF POLYMERS

The monomers can be polymerized either as such or mixed with others (copolymerization). It is also possible first to manufacture certain polymers

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[1] W. REPPE; see *Modern Plastics*, **23** (1945) 162.

and then convert them into others by chemical modification. The latter method is somewhat laborious, but sometimes offers advantages.

In all these processes the choice of the catalyst plays an important part. As auxiliaries to these, the *stabilizers* are also important, serving in particular to stabilize the monomers or the polymerizable intermediate products.

Generally, these stabilizers are reducing substances like phenol or hydroquinone, from which we may conclude that they destroy peroxide-containing intermediate products. Finally we mention the *polymerization regulators* which serve to control too quick or auto-catalytically accelerated reactions. Turpentine oil acts as such for the polymerization of acrylic compounds; its action is far from being completely understood.
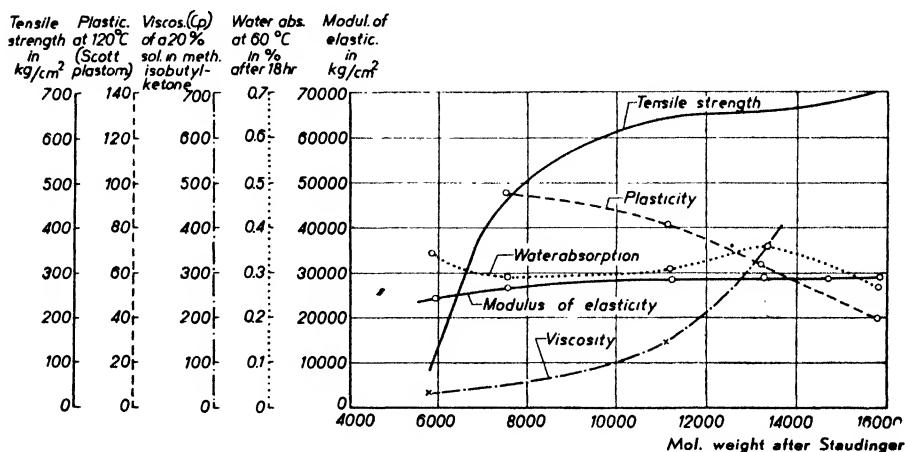
Fig. 69. The improvement in mechanical properties of polyvinyl chloride with increasing molecular weight.

As regards the mechanical properties of the final product, it is, generally speaking, desirable to achieve as high a degree of polymerization as possible, as shown in Fig. 69 (see also Fig. 30, p. 35).

a. Polymerization.

The polymerization is an exothermic reaction, in which from 15 to 30 kcal/mole of heat are freed. The great difficulties experienced in removing this quantity of heat have led to the development of the solution and the emulsion polymerization (p. 10), instead of the bulk polymerization.

As the formation of nuclei is the slowest of the three processes in the chain reaction (compare p. 4), the catalysts which accelerate the formation of nuclei are the most important. As such, peroxides (dibenzoyl peroxide),

SnCl$_4$, and BF$_3$ are to be considered. Also, light of short wave length can stimulate the polymerization, although it is not used in practice. In spite of the difficulties in connection with the removal of heat, the *bulk polymerization* is still applied in connection with the manufacturing of thick-walled objects made from acrylic and methacrylic esters. They are mechanically very strong, because the degree of polymerization is high (up to 150,000). They are of the
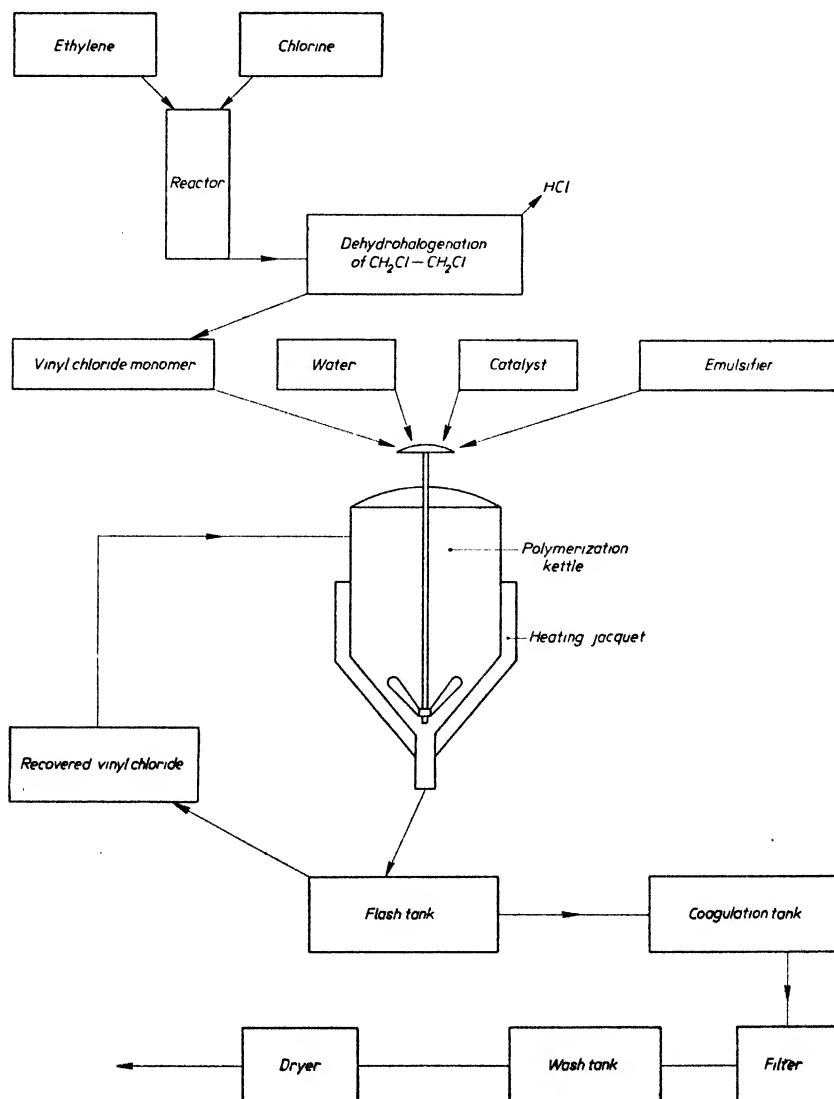
Fig. 70. Flow sheet of polyvinyl chloride.

greatest purity and transparency, which is important for optical purposes. With a view to this, the polymerization has to be conducted carefully and slowly, while at the same time dosing exactly the quantity of catalysts. For the manufacturing of sheets with a thickness of 0.5 mm and upwards, the liquid monomer material is polymerized preferably in flat glass containers, the walls of which can be moved towards each other during the polymerization process, with a view to compensating the shrinkage of about 20%. Sometimes a small quantity of the monomer can be pre-polymerized until the initial quick heat development is passed; then the rest of the monomer can be added as the polymerization process proceeds.

Fig. 70 presents a flow sheet for the production of polyvinyl chloride as an example of this type of process. The equipment is relatively simple, consisting of apparatus well-known in chemical technology (autoclaves, distillation columns, etc.), but requiring very great skill in operation.

A *continuous method* has been developed for producing polystyrene. At the bottom of a tower the material, which is viscous when hot, can be carried off while a continuous flow comes from above[1]. The cooled material is fed into a grinder which converts the polystyrene into granules.

Especially important for the manufacturing of tubes is also the centrifugal method, in which the polymerization is done in tubes which rotate at high speed round their longitudinal axes.

On page 8 attention was called to the heterogeneous degree of polymerization in a polymer. Often, some monomer is still present, and certain properties such as the heat resistance are consequently lowered considerably. By means of subsequent heating it is possible to remove these low polymer portions. Thus, as regards polystyrene, the heat resistance can be increased by about 15° C by heating it for 48 hours at 125° C (257° F). It is also possible to remove the low polymer portions by precipitation; in practice, however, this method is too expensive.

The *solution polymerization* is effected in boilers and the heat which is set free can be carried off easily because stirring is possible if care is taken that the solution is kept sufficiently diluted. The degree of polymerization reached depends on many factors: on the kind of solvent, on temperature, accelerator and dilution.

The principal difficulty is that it is almost impossible to bring about complete polymerization because the last portions of the monomer are too greatly diluted. It is also difficult to remove the solvent completely and therefore the solution polymerization is used as little as possible. An

[1] DUNLOP and REESE, *Ind. Eng. Chem.*, 40 (1948) 654.

improvement has been achieved by using solvents, which dissolve the monomer but not the polymer, so that the latter is eliminated automatically.

Emulsion polymerization is by far the most important process; it has been developed to a high technical degree. In modern factories the temperature is kept at the desired level by allowing cold emulsion to flow to, as the temperature increases. When the greater part has been polymerized, the residual monomer may be rapidly removed by deaeration or steam distillation.

The choice of the emulsifier is very important; soaps, ammonium oleate and similar materials are used. By regulating the temperature exactly, it becomes possible, within narrow limits, to choose the most desirable temperature and to finish the reaction very quickly. In this way it has proved possible to bring acrylic ester to complete polymerization within an hour's time.

The polymerisate, exactly as in the case of rubber latex, is often coagulated by adding electrolytes. The coagulum can be washed on rolls. Polymerizates which coagulate in grit form can be cleaned by centrifuging.

In order to avoid the often difficult removal of the emulsifiers and to facilitate the drying process, pearl polymerization (page 12) is used in certain cases.

b.   Copolymerization.

The possibility of copolymerization, mentioned earlier on page 12, has found its practical application especially in the case of the ethylene derivatives; polyvinyl chloride-vinyl acetate forms an example. It appears that the proportion of the two monomers in the different fractions fluctuates considerably (compare page 15) causing certain difficulties connected with the maintainance of the constancy of the properties. This is especially the case when the polymerization velocities of the monomers differ considerably from each other. In such cases this difficulty is overcome by adding the more quickly reacting monomer later on.

c.   Conversion of polymers.

It appears that certain polymers can be manufactured by the chemical transformation of other polymers. A well-known example is polyvinyl alcohol which is obtained from polyvinyl acetate in alcoholic solution with the aid of acid catalysts. In Fig. 71 the saponification of polyacrylic ester with KOH, forming a polyacrylic acid salt, is presented.

In general, it can be said that saponification, halogenation and similar operations known from low-molecular chemistry can be carried out easily in the case of high polymers provided a suitable contact liquid which dissolves,

both the polymer and the reagent can be found. If no chain rupture, cyclization, or other secondary reaction takes place, the molecular weight of the initial polymer is maintained. On page 67 we have already pointed out that

$$—CH_2—CH—CH_2—CH— \qquad\qquad —CH_2—CH—CH_2—CH—$$

Polyacrylic ester $\qquad + KOH \rightarrow \qquad$ Potassium polyacrylate
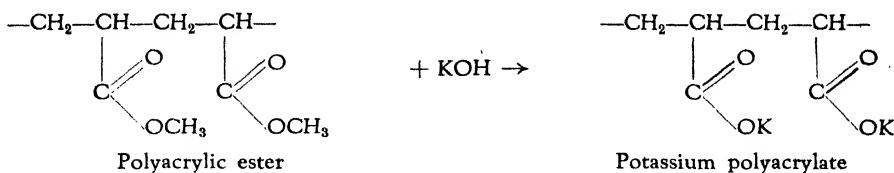
Fig. 71. Conversion of a vinyl polymer.

on this basis STAUDINGER supplied proofs for his views regarding high molecular structure.

The halogenation of polymers has found considerable application in Germany in connection with the so-called postchlorination of the polyvinyl chlorides which is discussed on page 114.

§ 32. POLYETHYLENE[1] (POLYETHENE) AND POLYETHYLENE TETRAFLUORIDE

From a chemical point of view, polyethene[1] is perhaps the simplest organic polymer that can exist, since it is nothing more than a high-molecular paraffin:

$$.... — CH_2 — CH_2 — CH_2 — CH_2 — .... \text{ polyethylene.}$$
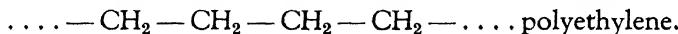
The polymerization of the monomer is carried out under the high pressure of about 1000 atm (200° C = 392° F), making the manufacturing conditions difficult.[2] Nevertheless production on an industrial scale has been developed since its discovery in 1933.

The product seems to consist of branched[3] chain molecules (Fig. 72) with a strong tendency to crystallize. The finished products show therefore mechanical properties reminding us to a certain extent of gutta percha, which is also strongly crystallized. If this crystallizing capacity did not exist, polyethylene would, without doubt, be a typical (non-vulcanizable) rubber.

$$...CH_2 — CH_2 — CH — CH_2 —...$$
$$| $$
$$CH_2$$
$$|$$
$$CH_3$$
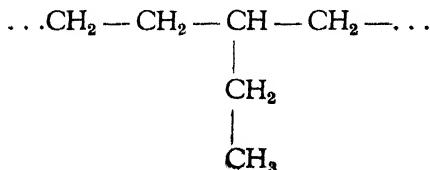
Fig. 72. Branched molecule of polyethene.

[1] See for a general description: E. HUNTHER, W. E. OAKES, R. B. RICHARDS, and E. L. MIDWINTER, Brit. Plast., 17 (1945) 94, 146, 208.
[2] For a detailed description see: Modern Plastics, 23 (1946) 141.
[3] R. HOUWINK, Brit. Plastics, 18 (1946) 192.

As a consequence of the chain form of the molecules, these can be easily oriented, leading to different properties in the "machine direction", compared with the perpendicular direction.

One would expect polyethene to dissolve easily in non-polar fluids. However, it is almost completely insoluble in all organic liquids below 60 °C (140 °F), and the swelling power is considerably less than for other polymers like polystyrene and polyisobutylene.

There is evidence that this peculiarity is to be ascribed to the high degree of crystallization (up to 75%,). In stretched natural rubber only about 25 % seems to be crystallized, and in gutta about 40 to 50%.

This is demonstrated [1] by Fig. 73, where the degree of crystallinity is plotted against temperature; above 120° C the last crystals disappear. The observation [2] that at 50° C polyethylene begins to dissolve in certain organic fluids (Fig. 73) is explained by assuming that at this temperature so many crystals have been melted that the factor U_{PP} (equation 11, page 51) is sufficiently reduced to make U_{LP} the more important.
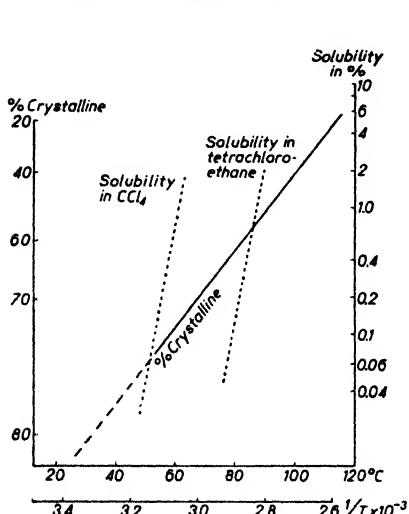
Fig. 73.. Change of crystallinity and solubility of polyethylene (logarithmic scales).

Being a paraffin, it is clear that polyethylene is unaffected by most chemicals. With polyisobutylene and polystyrene the polyethylene forms a group of materials with minimum dielectric losses of the order of $tg\delta = 2.10^{-4}$ (see Table 28). They are lower than for nonvulcanized rubber which is due to the double bond of the latter. For all materials considered in Table 28 the dielectric constant is low, being about 2.5. It is still higher than the ideal value of 1 (vacuum), so that some internal displacement does take place in all these dielectrics in an alternating field; probably this may be ascribed to the movement of electrons (electron polarization). The volume resistance is very high for all dielectrics mentioned here.

Strictly speaking, the resistivity should be infinite because pure organic nonpolar substances offer no opportunity for the conduction of an electric current. The fact that measurable values are found is due to impurities (stabilizers for the emulsion, etc.).

[1] R. B. RICHARDS, Trans. Faraday Soc., 41 (1945) 127.
[2] C. S. MYERS, Modern Plastics, 21 (1944) 103, 174.

TABLE 28.

ELECTRICAL PROPERTIES OF POLYETHENE IN COMPARISON WITH OTHER MATERIALS

	Volume resistivity (ohm.cm)	Dielectric constant	Power factor (tg δ in 10^{-4} at 10^6 cycles)
Polyethene	10^{17}	2.3	2
Natural rubber (unvulc.)	10^{16}	2.5	25
Natural rubber (vulc.)	10^{16}	3	20-100
Polystyrene	10^{15}	2.6	2
Polyisobutylene	10^{16}	2.3	10

The polyethylene resins now available soften rather sharply at about 110° C (228° F). In England they are sold under the name of Alkathene, in U.S.A. the generic name polythene is used, in Germany they were known as Lupolene. They remain flexible at very low temperatures even without addition of plasticizer. All mechanical operations usual for plastics, like calendering, extrusion moulding, and heat sealing, can be applied. A complication is caused by the high coefficient of expansion ($\lambda = 25.10^5$). When a piece is cooled from 115 to 25 °C (239 to 77 °F), the volume shrinkage is found to be 14%, which may lead to voids. Hollow articles can be made by blowing.

An outstanding feature is the low dielectric loss, already mentioned above. The chief applications of polyethylene are therefore to be expected in low loss cable insulations; radar has been largely promoted by this material. One would expect an unusually low water permeability in such a completely non-polar paraffin. It is therefore surprising that it is 300 times larger than that of polyvinylidene chloride (p. 117). The reasons for this are not yet clear.

Recently, *polyethylene tetrafluoride* has appeared on the market under the name of Teflon. It is a thermoplast distinguishing itself by an extraordinarily high temperature resistance, practically negligible dielectric losses (375° C = 730° F) and great chemical inertness. It does not swell in organic solvents and is not attacked by strong alkalis or strong acids but only by molten alkali metal, molten NaOH or steam above 200° C (392° F). Consequently the working up of the material is very difficult; it is compressed in powder form by high pressure at 130° C. At present the price is still too high for large scale industrial application.

§ 33. POLYMERS OF STYRENE, DICHLOROSTYRENE AND VINYL CARBAZOLE

Like polyethylene, polystyrene — CH_2 — CH — owes its importance

$$\overset{|}{C_6H_5}$$

largely to the fact that the molecule is a pure hydrocarbon[1] without dipole groups. It is used as an electric insulating material which is approximately equivalent to quartz or mica. Moreover, its ability to be coloured, its suitability to injection moulding (p. 96), its low specific gravity (1.05), and the very low price which may be expected in the future (Chap. XVI), suggest a bright future for this material.

A limit for the applicability is set, however, by the heat distortion temperature of only 75 °C (170 °F), which compared with 140 °C (280 °F) for phenol-formaldehyde products, is insufficient for many technical purposes. If it were technically possible to interlink the polystyrene in a suitable way, e.g., by means of p— divinylbenzene (page 53), then an ideal electrical insulating material would come into existence, which might replace Bakelite for many purposes. Such attempts have failed so far, but in Germany an attempt was made to increase the heat resistance by admixture of SiO_2 as a filler. The material then becomes brittle, however, and only a small gain in heat resistance is obtained. A better method is to convert the polystyrene into poly-(2,4)-dichlorostyrene — CH — CH_2 — , which has a heat distortion temperature of 112 °C (235 °F)
$\overset{|}{C_6H_3Cl_2}$
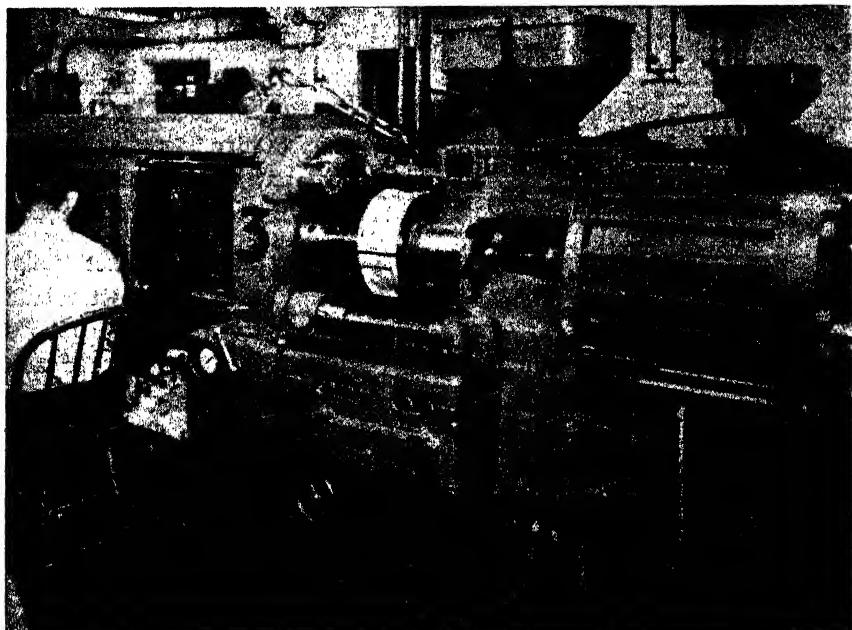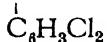
Fig. 74. Injection moulding machine.

[1] In order to avoid all ions in polystyrene, it is polymerized with H_2O_2 as a catalyst, which can be evaporated later on.

and possesses almost the same [1] excellent electric properties and low water absorption as polystyrene.

   In view of the importance of the injection moulding technique for the manufacturing of articles from vinyl polymers, especially from polystyrene, we show in Fig. 74 a machine for this purpose. The material comes out of the hopper, 1, and by means of a piston is pressed through the electrically heated cylinder, 2, and through a nozzle into the water cooled mould, which is adjusted at the spot indicated by 3. This mould is automatically closed and opened by an electric motor; at the same time the piece thus formed is ejected. Fig. 75 shows a large injection moulded article (diam. 11 inches) made of polystyrene. On account of the relatively sharp softening point of the poly-styrene, the solidification, after injection, takes place within a narrow range of temperature; therefore the working speed is very great.
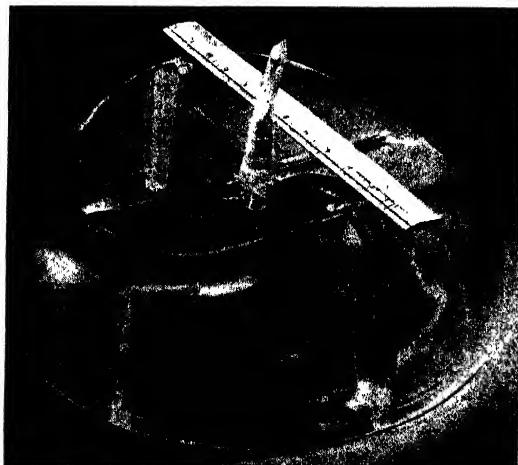
Fig. 75. Large injection moulded polystyrene article.

Fig. 76. Blowing a bottle from polystyrene (Courtesy Plax Corp.).

   Overheating should be avoided, because then decomposition phenomena set in, leading to cavities and capillary cracks.

   The polystyrene is transparent like glass, but with the aid of dyes, which can best be incorporated on the rolls, it is obtained with beautiful colours. This property had led to numerous applications, of which we mention: tube closings, deluxe packings, fountain pens, furniture fittings, etc.

[1] C. L. JONES and M. A. BROWN, Modern Plastics, 21 (1944) 93, 168.

On page 94 it was mentioned that a technique has recently been developed for blowing hollow articles like bottles and that polystyrene is especially suited [1] for this purpose. Although this process is still in its beginning, we show a picture of it in Fig. 76, because in the future this may lead to extensive applications.

Although the application as a moulded piece is the most important one, a demand for polystyrene foils has sprung up, especially for electrotechnical purposes, e.g., as a substitute for mica in condensor dielectrics. In this connection the experience, known already from other industries, of improving the mechanical properties by orientation (see page 45) has been applied. Under the name of "Styroflex", foils with a thickness of 0.02 to 0.15 mm with a tensile strength of 700 kg/cm² (10,000 p.s.i.) and an extension at break of 4%, were used in Germany. With a view to obtaining a cable insulation with as low dielectric losses as possible, styroflex is wound up quite loosely and provided with air pockets.

Of course, polystyrene can also be used in the electrical industry for insulating lacquers and for impregnating paper (foils) etc; for this purpose it can be dissolved in benzene. In order to avoid the loss of volume which occurs while expelling the solvent, monostyrene can be polymerized right on the spot. To make shipping and storing possible, the monomer is put on the market provided with a stabilizer which can be removed by washing out before use.

Poly-dichlorostyrene [2] — CH₂ — CH — is considerably more heat resis-

tant and tougher than polystyrene. In the latter respect it lies between polystyrene and cellulose acetobutyrate, as is seen from Table 29. The better heat
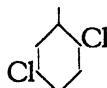
TABLE 29.

SOME PROPERTIES OF POLY-DICHLOROSTYRENE [3]

	Poly-dichloro-styrene	Polystyrene	Cellulose acetobutyrate
Distortion under heat, °C	115—130	75—90	45—100
°F	240—265	165—190	115—215
Injection moulding temp., °C	245—275	160—260	170—215
°F	475—525	325—500	340—420
Impact strength (notched) ft. lb/inch	1.0—1.5	0.25—0.4	0.5—7.5

[1] See J. BAILEY, *Modern Plastics*, 22 (1945).
[2] Other chloro-styrenes of practical value are mono-p-chlorostyrene and tri-chlorostyrene. Chlorine can also be substituted by fluorine.
[3] J. C. MICHALEK and C. C. CLARK, *Chem. Eng. News*, 22 (1944) 1559.

resistance results in a higher moulding temperature, which, however, is still within practical limits. This rather new material doubtlessly offers attractive prospects, especially since the electrical properties are — as to be expected — of the same order as those of polystyrene.

The need of an electrical insulating material with a high heat resistance is also met by *polyvinylcarbazole:*

$$-CH_2-C-$$

,
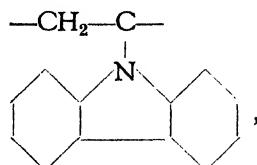
which has been used for injection moulding in Germany.

Because of the difficulties in moulding, its high price and its poor mechanical properties (due to its pronounced fibrous structure) it cannot compete with the phenol-formaldehyde materials. The dielectric losses (tg $\delta = 10^{-3}$) are similar to those of polystyrene, but the impact resistance in the direction of orientation is too low for most applications. For this material a considerably higher injection temperature up to 270 °C (518 °F) is required than for polystyrene.

Polyvinylcarbazole can also be supplied in profile-, tube-, and rod-form; naturally here the influence of the orientation is very strong.

§ 34. POLYVINYL CHLORIDE, POLYVINYLIDENE CHLORIDE AND POLYVINYL ACETATE

Polyvinyl chloride[1], — $CH_2 — CH —$, is used as such in industry, but

$$|$$
$$Cl$$

mostly it is copolymerized with *vinylidene chloride* — $CH_2 — C —$, *vinyl*

$$|$$
$$Cl_2$$

acetate — $CH_2 — CH —$, etc. In Fig. 94 p. 103 it was already shown how

$$|$$
$$OCOCH_3$$

the properties depend on the molecular weight.

Regarding the structure of copolymers of vinyl chloride and vinyl acetate it has been shown[2] that vinyl chloride enters into the chain more rapidly than does vinyl acetate, the ratio of the rates depending on the polymerization temperature. Since relatively more chloride is used in the beginning, chains of widely different composition are formed. They range from chains richer

A detailed summary of the properties of vinyl plastics is given by H. L. DRUKKER,
[1] *Symposium on Plastics*, Amer. Soc. Test. Mat., Philadelphia 1944.
[2] C. S. MARVEL et al. *J. Am. Chem. Soc.*, 64 (1942) 2356.

in chlorine than the monomer mixture in the beginning to chains richer in acetate towards the end of the polymerization.

The applications have been developed in two directions: as hard and as soft rubbery materials, the latter obtained by adding plasticizers. In the latter case we meet a typical example of external softening, the principles of which were discussed on page 59.

The *hard* polyvinyl chloride was especially developed in Germany under the name of "Vinidur". It contains no acetate and in order to increase its
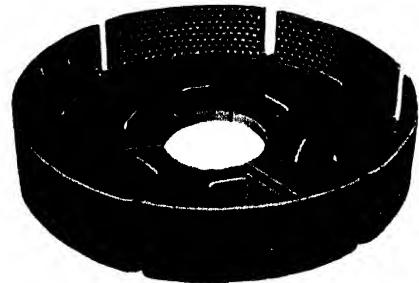
Fig. 77. Sieve for chemical purposes, made from hard PVC.
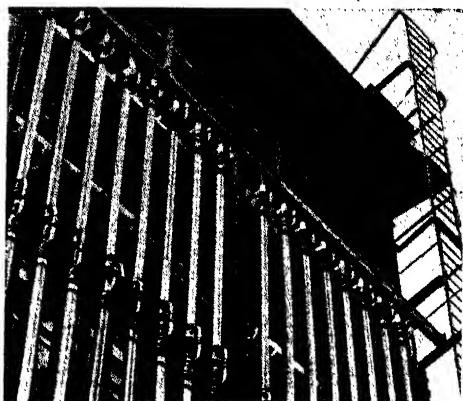
Fig. 78. Hard PVC tubes for transporting acids.

solubility in certain solvents and its strength the chlorine content of 55% was increased to 65% by after-chlorination in solution. A molecular weight of about 100,000 is usual for many applications, of which one is shown in Fig. 77. The chemical resistance also leads to a demand in the form of tubes (Fig. 78). This application is however restricted by the low heat resistance; 40° C (104° F) is the limit for many purposes. A first method to overcome these difficulties is by increasing the wall thickness (see p. 117). A higher limit is reached by lining metal tubes with vinyl chloride and this has led to important applications. These have been extended by lining tanks, buckets, and other containers for the chemical industry. For this purpose sheets of the vinyl chloride are glued on the walls of the tank which are heated from the outside by means of a flame and which have first been coated by a solution of the polymer. The seams are heat sealed by applying strips of the polymer. A special high frequency apparatus has been developed to detect leaks in the lining and in this way a high quality can be guaranteed. Among other applications of hard polyvinyl chloride and its copolymers may be mentioned: slide rules, drafting instruments, unbreakable sound recording discs, battery

separators, etc; also fibres and fabrics. For the properties of such fibres see Fig. 175.

A difficulty in the processing of the hard vinyl chlorides is that the decomposition temperature is in the neighbourhood of the softening temperature, so that the working up must be done quickly and with the aid of heavy machines, because the material is not sufficiently plastic. Making it more plastic would lead to decomposition. In Fig. 79 a picture [1] of the situation is given.

For making rods or tubes it must be first heated on rolls to 160° C (320° F) and then quickly extruded by flash heating to 190° C (374° F).
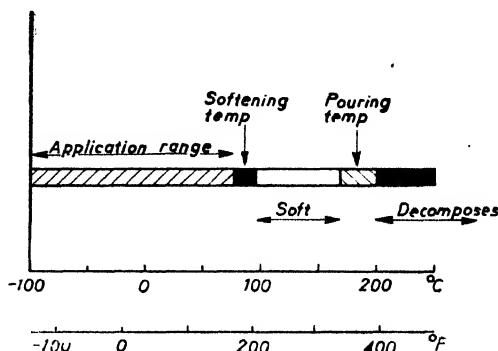
Fig. 79. Decomposition temperature and working- up ranges of polyvinyl chloride.

For thin films of 1.0 to 1.4 mil thickness (called luvitherm) it is rolled while hot at 165° C (329° F), transferred to a calender for filming at the same temperature and heated for a few seconds on a roll at 260° C (500° F). Then it is stretched about 270% on a roll heated to 120° C (250° F). The effect of the stretching shows itself in the difference in strength in both directions; lengthwise the tensile strength is 1200 kg/cm² (17,000 lb/inch²) crosswise only 400 kg/cm² (5700 lb/inch²); the elongation is 15—30 and 5% respectively in the two directions. This type of film has been used for packaging under tropical conditions.

The high temperatures mentioned cause a slight deterioration of the polyvinyl-chloride, leading to a brown or black colour. In order to overcome these difficulties, special extruders have been designed [2]; temperatures up to 177° C (350° F) are still necessary however. For moulding purposes the so-called impact compression moulding technique, has been developed, whereby the material is forced into the mould by means of a blow (see p. 95). In most cases, however, it is easier to machine articles from extruded profiles.

In the Anglo-Saxon countries more attention has been paid to the *plasticized polyvinyl chloride*, mostly copolymerized e.g. with vinylidene chloride and vinyl acetate. Up to 40 or 60 per cent of plasticizers like tricresyl phosphate, dibutyl phthalate, dibutyl sebacate, etc. render the material remarkably rubbery. The problem is to keep the range between temperature of flow and freezing temperature as large as possible. This can also be influenced by the ratios of the copolymers. The most important types contain at present 80—95 per cent

[1] K. Tensi and W. Zebrowski, *Brit. Plastics*, **18** (1946) 238.
[2] *Plastics Catalog*, New York 1945, p. 494.

of chloride; the acetate acts as an internal plasticizer (see p. 95). Compounding ingredients (carbon black, clay) can be added either to make the products cheaper or to provide specific properties. Vinylidene chloride is usually used as a copolymer in order to improve the processing and the compatability.

The materials can be calendered into films or sheets, extruded, moulded and heat sealed, as is to be expected from a thermoplastic.

The most promising applications are those, in which the material has a large surface (films), especially, when it is coated on a supporting layer (artificial leather).

The supporting layer prevents large extensions, which would lead to plastic deformations, because the materials are not vulcanizable. The large surface makes competition with natural rubber possible, the latter being oxidized, thus becoming hard and bad smelling (rain coats). In our opinion it is doubtful whether in future the competition with rubber will be possible for applications, in which the special properties are not significant [1]. For this reason the application to shoe soles and cable coverings (Fig. 80), etc. seems to show little promise. Notwithstanding this, there is a large market for fancy articles, seat covers, curtains, artificial leather, packaging and for chemical purposes.

A copolymer of the chloride with the acetate is used as a flexible fibre. Its wet strength is as great as its dry strength; the water repellency, the resistance to moth and to putrefying make it very attractive for special applications. Another copolymer with good fibre characteristics is that consisting of vinyl chloride, acrylonitrile and fumaric nitrile.

Fig. 80. Applications of softened polyvinyl chloride.

[1] Natural rubber and G.R.S. are expected to sell in future at about 15 ₵ per lb, plasticized vinyl chloride polymers at about 20 ₵ per lb. Taking into account their high specific gravity of 1.35 and the method of processing, they will be roughly 60 per cent more expensive, calculated by volume.

The polymers are available in the form of latex, which make coating processes very easy. The coagulum, however, consists of discrete particles which must be fluxed by exposing them to a temperature of about 143° C (290° F) for a short time in order to obtain a closed film.

Polyvinylidene chloride can be obtained by adding chlorine to ethylene and by subsequent polymerization. The present standard material has a softening point of 115—138° C (240—280° F); a wide variation is possible by changing the molecular weight and by making copolymers. The material crystallizes easily. By extruding, a high degree of orientation is obtained, which gives a 5-fold increase of strength up to 2800 kg/cm² (40,000 psi), a point of importance in making artificial ratan, for instance. Filaments are woven into corrosion-resistant insect screens. Films of vinylidene chloride can be heat sealed and excel in having a very low permeability to water vapour, this being due especially to the low solubility of water in the film (see page 85).

Polyvinylidene chloride can be injection moulded and extruded in large tubes. Fig. 81 shows the maximum working pressure which can be allowed [1] in such tubes assuming a safety factor of 5. Such tubes excel in their resistance to acids, alkalis, water, and many organic solvents.

Polyvinyl acetate as such has found fewer applications than the chloride, due to its lower heat distortion temperature. It is used for lacquers, adhesives, artificial leather and for bonding cellulose fibres, wood, leather, cork, etc. For these uses, the emulsions are cheapest. They

Fig. 81. Maximum working pressure in polyvinylidene tubes (safety factor = 5).

can be mixed with other compounds, such as starch solutions, rubber latex, asphalt or paraffin emulsions, etc.

Thanks to their excellent adhesive capacity, the polyvinyl acetates are competing with the polyacrylic esters for safety glass. For the manufacturing

[1] C. B. BRANCH and D. L. GIBB, *Modern Plastics*, 19 (1942) 64.

of this glass, solutions of the polymer containing plasticizer are coated on glass plates and are dried slowly in order to avoid the formation of bubbles. After the last of the solvent has been removed by vacuum, the next glass layer is pressed on in a hydraulic press.

§ 35. POLYACRYLATES

The most important representatives of this group are the polymers of acrylic acid, methacrylic acid and their esters.

$$\begin{array}{ccc} & H & \\ & | & \\ -CH_2 - & C - & \\ & | & \\ & COOH & \end{array} \qquad and \qquad \begin{array}{c} CH_3 \\ | \\ -CH_2 - C - \\ | \\ COOH \end{array}$$
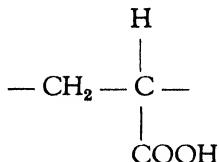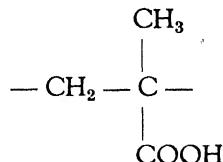
polyacrylic acid   polymethacrylic acid

These substances and their copolymers show certain similarities to polyvinyl chloride and polyvinyl acetate. In their applications they compete with the latter.
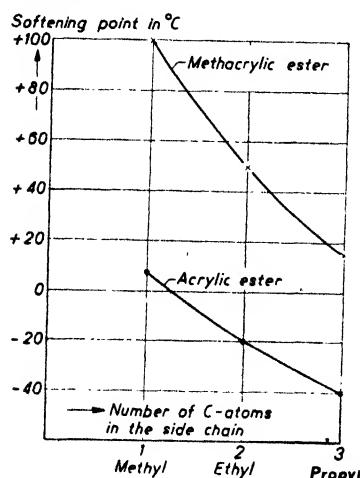
Fig. 82. Decrease of the softening point of the acrylic esters with increasing length of the side chains.

The methyl, ethyl and butyl esters are technically important but, considering Fig. 162, it can be expected that the secondary cohesion between the molecules will decrease as the side groups become longer. Fig. 82, in fact, shows that, the longer the side chains the more easily do the esters soften, and it appears immediately that the methacrylic ester of the polymerization degree contemplated here — with still longer side-chains than C_3 — will be a liquid.

The polymers, especially methacrylic acid methyl ester, are in general suitable as lacquers and glues, and also for the manufacturing of articles by moulding or preferably by injection moulding.

The mechanical and thermal properties are comparable to those of polystyrene (see Table 25); however, the electrical properties in the alternating field are considerably worse, due to the polar groups. The methacrylic acid methyl ester (Plexiglas, Perspex, Lucite) owes its prominent position to its *optical* properties; the combination of its great transparency (99%), its low specific

weight (1.18), its non-brittleness and its ability to be easily formed and machined (Fig. 83) by sawing, drilling, etc. has opened the road to many applications. If this material also possessed the hardness of glass and consequently should be scratchproof, an extraordinary future would open to it. However, in order to achieve this, a thorough interlinking of the chain molecules is neces-
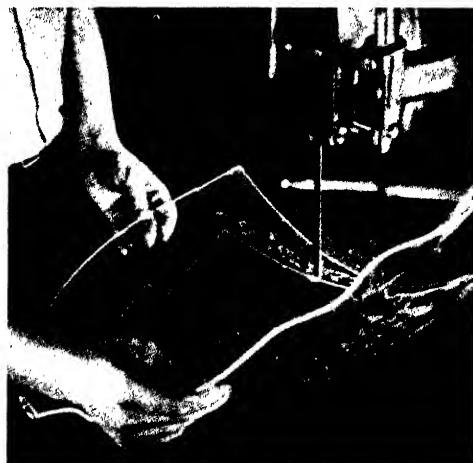
Fig. 83. Easy machining of Plexiglas.

Fig. 84. Aeroplane windows of Plexiglas.

sary (see Table 14, page 37). This is confirmed in the case of the phenol-formaldehyde resins in the C state (moulded resits) which are more scratch-proof. Whether, however, the other favourable properties like the impact strength and the possibility of being easily machined would not be lost remains to be seen. In any case, its application has so far been restricted to purposes in which the possibility of scratching is relatively limited, as in the case of aeroplane window panes (Fig. 84). In view of the application for curved transparent shield the forming technique is of special importance. The sheets become soft when heated in an oven above 105° C (220° F). They are then carefully placed in a mould made of plaster, plywood or metal covered with soft flannel. Often the weight of the sheet itself is sufficient for the forming operation. For deep curves, pressure is necessary, which can be applied by hand, mechanically or by air (cf. low pressure moulding, p. 166). Welding can be effected at 350° C (660° F); high frequency heating is often applied here.

In cases where the windows have to be scratch-proof (motorcar window panes) we have still to content ourselves with laminated safety glass, in which the outer layers of silica are glued together with acrylic esters or other polymers.

Fig. 85. Artificial denture made from poly-methacrylic acid methyl ester.

For apparatus requiring minute optical parts, a limitation is due to the low resistance to deformations in consequence of which distortions occur easily. All in all, it seems that Plexiglas and inorganic glass are satisfactory complements to each other. Another important field for its application is for artificial dentures (Fig. 85); in this respect the acrylic acid ester competes with polyvinyl chloride. A very simple method of making dentures is by hardening a mixture of low and high molecular methacrylic esters in a mould at low temperature in boiling water.

The chemical stability has led to a series of applications in the chemical industry. For lacquers, the polyacrylic acid esters are mostly used, mixed with other raw materials which at the same time fulfil the part of a plasticizer; the methacrylic acid ester, however, can yield films of excellent quality without any additions. As special fields for its application, we may mention: varnishing of light metals, artificial leather and wire. Naturally, the aqueous emulsions are also used for varnishing and adhesion purposes, amongst which should be mentioned especially the priming of leather, the manufacturing of leather substitutes, the covering of brick walls and the finishing of textiles for the manufacture of washable textile finishes.

The highly elastic representatives are hardly to be considered as rubber substitutes (see Table 35 page 138) because the materials cannot be vulcanized.

§ 36. POLYVINYL ACETALS AND VARIOUS OTHER VINYL DERIVATIVES

Polyvinyl acetals are derived from polyvinyl acetate by hydrolysis of the latter to the corresponding alcohol, which is then added to the aldehyde (Fig. 86):
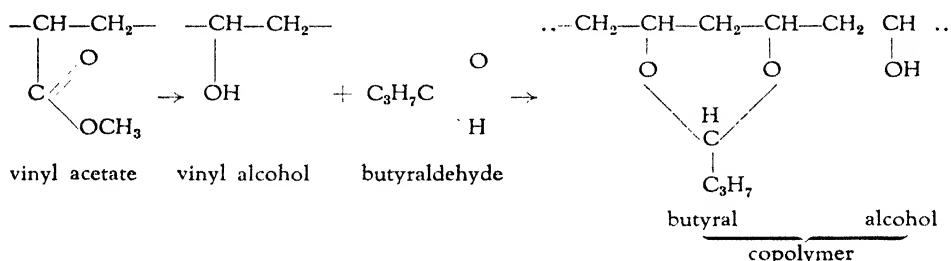
Fig. 86. Formation of a copolymer between polyvinyl butyral and polyvinyl alcohol.

The acetals exist in different types, according to the aldehyde which reacts with polyvinyl alcohol. Those best known are the formal, the acetal and the butyral. The hydrolysis and the condensation process may be conducted either as separate operations or together in the same reaction-bath. The reaction is not always carried out to completion, because often acetyl and hydroxyl groups are desirable in the final product.

Polyvinyl *formal* is used for wire enemals owing to its high softening temperature. The *acetals* find applications for moulding and injection moulding purposes. Most important are *polyvinyl butyral* and its copolymers. Since it contains a relatively high percentage of unreacted hydroxyl groups it is used as a safety glass interlayer, thanks to its flexibility and perfect adhesion to glass. When it is more completely acetalized, it is more compatible with plasticizers and is used in adhesives and in coated fabrics. Polyvinyl butyral can be run on ordinary rubber machinery, which facilitates its industrial application; calendering, frictioning, tubing and moulding are easily carried out. It can be interlinked, thus leading to a "curing process", by exposure to hot air at 132° C (270° F) during one hour.

The products recover less quickly after deformation than rubber. Like vinyl chloride they offer in coatings the advantage of much better weathering properties than rubber. Data [1] for the tensile strength of 110 kg/cm² (1500 lb/inch²) and an extension at break of 300% show that reasonable mechanical

[1] D. S. PLUMB, *Ind. Eng. Chem.*, 36 (1944) 1035.

values can be obtained (compare Table 35 p. 138). The coatings do not crack at —60° C (—76° F) and do not stick at 250° C (482° F); these are definite advantages compared with nitrocellulose. They are used for raincoats, etc.

Allyl alcohol $CH_2 = CH$ has become an important raw material for
$\qquad\qquad\qquad\qquad |$
$\qquad\qquad\qquad CH_2OH$
making unsaturated polyesters and unsaturated polyethers. In practice, ester-ification is carried out (Fig. 87) with, for example, a dicarboxylic acid like phthalic acid, leaving two free vinyl groups in the condensed product.

On heating, the material is converted into a water-white transparent ther-mosetting resin by virtue of these double bonds, that is, without water

phthalic acid anhydride   allyl alcohol
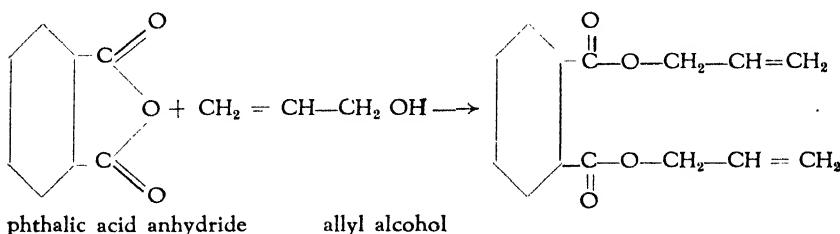
Fig. 87. Condensation to form an unsaturated polyester.

being split off, the latter being a source of much trouble in other thermosetting resins (see page 154). This opens remarkable possibilities with regard to the low pressure moulding technique and also for making reasonably scratch-proof glass.

These resins will be discussed in detail on page 192.

Polyvinyl alcohol is soluble in water and this feature leads to special appli-cations. It is used as a protective colloid, as sheets, films, coatings, rods and tubes. Its adhesion and ability to form tough and flexible films render it adaptable as a sizing for textile fibres. With glycerine, a rubbery mass can be obtained which is used for lining oil-resistant hoses.

Polyvinyl ethers are used as adhesives, impregnating agents and lacquers. They were developed in Germany (Igevin) but not used in the Allied countries. The ethers were made in Ludwigshafen by a continuous process by the addition of alcohol to acetylene [1], with a yield of 95 per cent (7000 tons p.a.).

The isobutyl and methyl ethers were the most frequently used.

Polyisobutylene is classed as a rubber and will therefore be discussed on p. 141.

[1] G. M. KLINE, *Brit. Plastics*, **18** (1946) 106.

CHAPTER VII

SYNTHETIC RUBBERS [1]

On page 42 it was explained why, in view of the rubbery high elasticity, it is necessary that certain parts of the macromolecule be able to execute a micro BROWNIAN motion, but that the macro BROWNIAN motion of the entire chain be prevented. It was found that, in particular, the hydrocarbons with 4 C atoms in the main chain (butadiene, isoprene, dimethylbutadiene, chloroprene and certain of their copolymers) show these properties. Apart from these, there are some other rubbery polymers which are not (thiokol) or not yet technically important (silicones, see Chap. XIV, polyesters, see page 189). Polyvinyl chloride can be made rubbery by the addition of plasticizers (see page 115); this is the so-called external plastization.

§ 37. RAW MATERIALS; THE MANUFACTURE OF MONOMERS

On page 21 we have already shown the formulae of the synthetic rubbers which for practical purposes are the most important ones; in Table 30 their monomers have been compiled.

From a commercial point of view, the correct choice of raw material is of decisive importance for the manufacturing of synthetic rubber; we shall see that the various countries use different raw materials [2] depending on their natural resources.

a. The manufacture of butadiene.

At present there are three principal methods of manufacturing butadiene, namely: from grain or potatoes, from petroleum, and from coal.

1. *From grain or potatoes.* From starch, ethyl alcohol is manufactured by fermentation. This is passed over Al_2O_3 or ZnO heated at 400 to 500° C (780 to 960° F), where it is dehydrogenated. (LEBEDEV process).

$$2 \ C_2H_5OH \longrightarrow \overset{H_2 \ \ H \ \ H \ \ H_2}{C=C-C=C} + 2H_2O+H_2$$
$$\text{alcohol} \qquad \text{butadiene}$$

Lebedev process for making butadiene.

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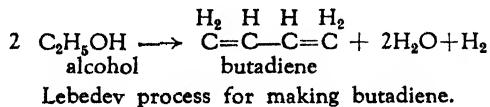
[1] For comprehensive treatments: H. BARRON, *Modern Synthetic Rubbers*, London 1945; W. J. S. NAUNTON, *Synthetic Rubber*, London 1937; F. MARCHIONNA, *Butalastic Polymers*, New York 1946.

[2] See for a comparison of the three Buna processes in Germany: A. HAEL, *Rev. gén. caoutchouc*, **25** (1948) 268.

TABLE 30.

MOST IMPORTANT SYNTHETIC RUBBERS

Monomer		Name of the final product
$\begin{matrix} H_2 & H & H & H_2 \\ -C-C=C-C- \end{matrix}$	Butadiene	SKA, SKB, Numbered Bunas.
$\begin{matrix} H_2 & H & H & H_2 & H_2 & H \\ -C-C=C-C-C-C- \end{matrix}$ (with benzene ring)	Copolymer of 5 mole of butadiene and 1 mole of styrene	GRS, Buna S.
$\begin{matrix} H_2 & H & H & H_2 & H_2 & H \\ -C-C=C-C-C-C- \\ & & & & & | \\ & & & & & CN \end{matrix}$	Copolymer of butadiene and vinyl cyanide	GRA, Perbunan, Nitrile rubber.
$\begin{matrix} H_2 & Cl & H & H_2 \\ -C-C=C-C- \end{matrix}$	Chloroprene	GRM, Neoprene.
$\begin{matrix} H_2 & CH_3 \\ & | \\ -C-C- \\ & | \\ & CH_3 \end{matrix}$	Isobutylene, usually copolymerized with isoprene	GRI, Vistanex, Butyl rubber.
$\begin{matrix} & & S & S \\ H_2 & H_2 & \| & \| \\ -C-C-S-S- \end{matrix}$ or $\begin{matrix} H_2 & H_2 & H_2 & H_2 & H_2 \\ -C-C-O-C-O-C-C-S-S- \end{matrix}$	Ethylene tetrasulphide	Thiokol, Perduren.
$\begin{matrix} CH_3 \\ | \\ -Si-O- \\ | \\ CH_3 \end{matrix}$	Silicone	Silicone.
$\begin{matrix} H_2 & H \\ -C-C- \\ & Cl \end{matrix}$	Vinyl chloride (plasticized)	Polyvinyl chloride, Koroseal, Vinylite, etc.

Although this process is still applied in agricultural countries (Russia), it is doubtless more expensive than that starting from petroleum. Data are available[1] showing that the cost of butadiene from alcohol will, in the future, be 8.8 ¢ per lb, against 6.4 ¢ for the petroleum process. In the U.S.A., therefore, the alcohol-butadiene plants have been discontinued.

2. *From coal.* In this connection there are three possibilities. Two of these start from acetylene, made from calcium carbide and water; the third one uses benzene from the coke works. These three methods are as follows:

[1] *Progress Report, War Production Board,* 12428, Washington 1944.

a. The shortest route from acetylene to butadiene is that indicated by NIEUW-LAND. First, vinyl acetylene is produced by combining two acetylene molecules and then   reducing it to butadiene.

$$CH{\equiv}CH \longrightarrow CH{\equiv}C{-}CH{=}CH_2 \longrightarrow CH_2{=}CH{-}CH{=}CH_2$$
$$\text{acetylene} \qquad \text{vinyl acetylene} \qquad\qquad \text{butadiene}$$
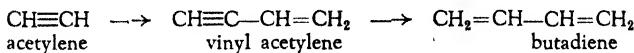
β. In Germany a different method is used. Water is added to acetylene, thus forming acetaldehyde.

$$CH{\equiv}CH + H_2O \longrightarrow CH_3{-}C{\overset{\displaystyle O}{\underset{\displaystyle H}{}}}$$
$$\text{acetylene} \qquad\qquad \text{acetaldehyde}$$
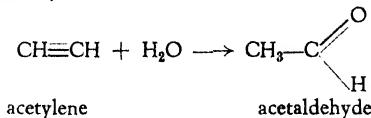
Two molecules in the presence of alkali form aldol, which is reduced to 1,3-dihydroxybutane and then converted into butadiene by splitting off water:

$$2\ CH_3C{\overset{O}{\underset{H}{}}} \rightarrow CH_3C{\overset{OH}{\underset{H}{}}}{-}CH_2{-}C{\overset{O}{\underset{H}{}}} \rightarrow CH_3{-}C{\overset{OH}{\underset{H}{}}}{-}CH_2{-}CH_2OH \longrightarrow CH_2{=}CH{-}CH{=}CH_2$$
$$\text{acetaldehyde} \qquad \text{aldol} \qquad\qquad\qquad \text{1,3-dihydroxybutane} \qquad\qquad \text{butadiene}$$
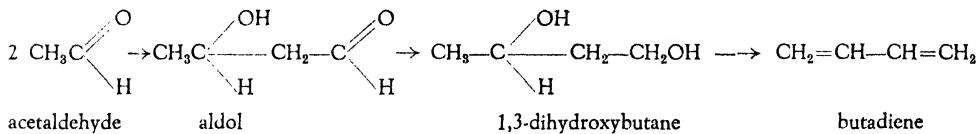
γ. The third method starts from benzene, obtained by distillation of coal. The benzene is reduced to cyclohexane which, when heated, decomposes into ethylene, butadiene, and hydrogen.

$$C_6H_6 + 3H_2 \longrightarrow C_6H_{12} \longrightarrow C_4H_6 + C_2H_4 + H_2$$
$$\text{cyclohexane} \quad \text{butadiene ethylene}$$
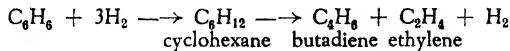
3. *From mineral oil.* By cracking petroleum, butane is obtained which is first reduced to butylene and then to butadiene. The output of this reaction seems to be of the order of 5% only.

$$CH_3{-}CH_2{-}CH_2{-}CH_3 \longrightarrow CH_3{-}CH_2{-}CH{=}CH_2 \longrightarrow CH_2{=}CH{-}CH{=}CH_2$$
$$\text{butane} \qquad\qquad \text{butylene (butene)} \qquad\qquad \text{butadiene}$$
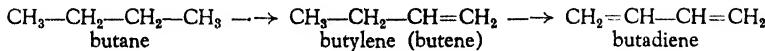
This process finds application not only in America, but also in Russia. It is also possible to make butadiene directly from methane.

b.   The manufacture of styrene.

Styrene is manufactured by first adding ethylene to benzene and then dehydrogenating the ethyl benzene by heating in the presence of superheated steam or by cracking at 700° C (1220° F).

c. The manufacture of vinyl cyanide.

This can be made from ethylene oxide by reaction with HCN. Ethylene cyanohydrin is formed, which at 260° C (500° F) is catalytically dehydrated to vinyl cyanide.

$$CH_2—CH_2 + HCN \longrightarrow CH_2OH \qquad \overset{—H_2O}{\longrightarrow} \qquad CH_2 = CH$$
$$\underset{O}{\diagdown \diagup} \qquad\qquad\quad \underset{CH_2CN}{|} \qquad\qquad\qquad \underset{CN}{|}$$

ethylene oxide   ethylene cyanohydrin   vinyl cyanide
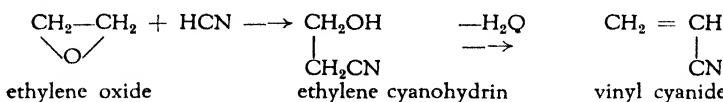
Fig. 88. The formation of vinyl cyanide.

d. The manufacture of chloroprene.

For the manufacture of chloroprene, the NIEUWLAND method, mentioned under 2 *a*, is applied for producing vinyl acetylene, which then adds on HCl. This process seems to be developed to such an extent that 1 lb. of acetylene produces 1 lb. of neoprene.

$$CH\equiv C—CH = CH_2 + HCl \longrightarrow CH_2 - C—CH = CH_2$$
$$\underset{Cl}{|}$$

chloroprene (2-chloro-1-3-butadiene)
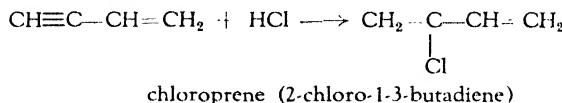
e. The manufacture of isobutylene.

Isobutylene is formed by cracking mineral oil or by splitting off water from isobutyl alcohol.

$$\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{CH—CH_2OH}}}} \longrightarrow \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C=CH_2}}}} + H_2O$$

isobutyl   isobutylene
alcohol
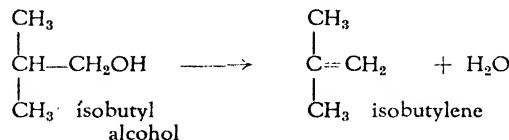
Isobutyl alcohol is formed as a by-product of the synthesis of methanol from CO_2 and H_2.

f. The manufacture of ethylene polysulphide.

Ethylene polysulphide is manufactured by mixing ethylene dichloride with an aqueous solution of sodium polysulphide.

$$CH_2Cl—CH_2Cl + Na_2S_x \longrightarrow —CH_2—CH_2—S—S— + NaCl$$
$$\underset{S}{\overset{||}{}} \underset{S}{\overset{||}{}}$$

ethylene dichloride
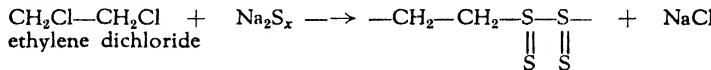
g. The manufacture of silicones (see Chap. XIV; for vinyl chloride see page 101).

When critically surveying this series of reactions, it appears that the following substances occupy key-positions (being necessary for the manufacture of at least one kind of synthetic rubber): ethyl alcohol, acetylene, ethylene, benzene, mineral oil and isobutyl alcohol.

§ 38. POLYMERIZATION AND FURTHER MANUFACTURING PROCESSES

At the present time, polymerization is usually carried out in emulsion (see page 11) ; Fig. 89 shows an installation used for the manufacturing of GRS.
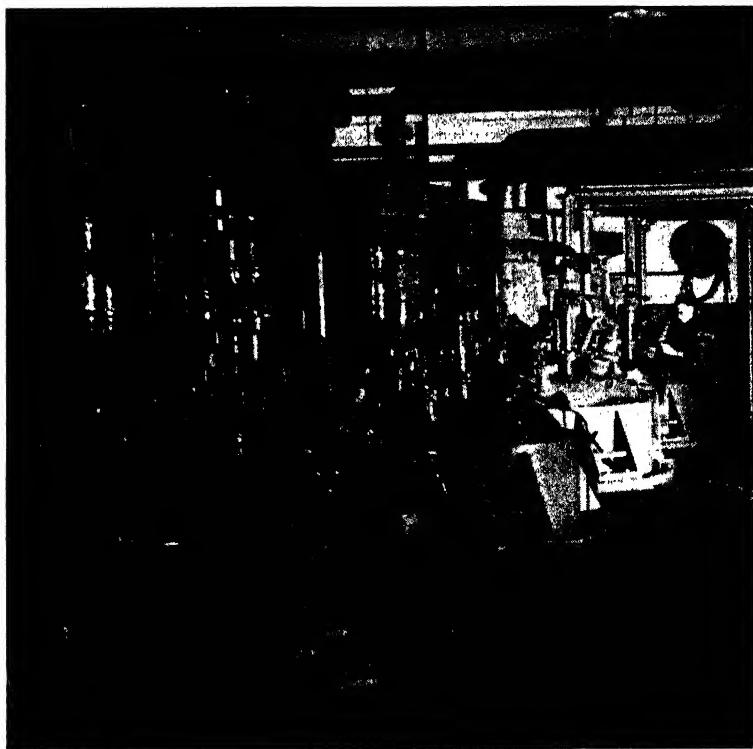
Fig. 89. Series of reactors for the polymerization of GRS.

The *polybutadienes*, which in Germany are known as numbered Bunas (Buna 32, Buna 85, Buna 115, etc.), are now manufactured on a large scale only in Russia under the designation of SKA[1] and SKB. Little is known about the way in which the Russians carry out the polymerization technically. Concerning the *polymethyl butadienes*, the methyl rubbers H (hard) and W (Weich = soft) were developed in Germany during the first world war.

The *copolymers of butadiene* have become much more important, especially the types G R S (Government Rubber, Styrene type) and G R A (Government Rubber, Acrylonitrile type), developed in Germany under the names Buna

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[1] SK is the abbreviation of Sintetisckeskij Kauchuk.

S and Buna N, respectively. Buna means a product obtained by polymerization of *butadiene* with the aid of *natrium* (= sodium).

G R S (Buna S) is a copolymer, the base molecule of which contains about one unit of styrene per five units butadiene, corresponding to a styrene content of roughly 30% by weight.

The polymerization can be effected in two different ways.

In the first method, the process is carried out separately in each reactor of a group. In the second the emulsion is run through all the reactors of a group and thus a continuous process is obtained. The polymerization is stopped when roughly 70% is converted. The unreacted monomer is removed and added to the next run. The process is controlled by measuring the plasticity of the polymer in a MOONEY plastometer. Usually, the reactors have a content of between 8,000 and 15,000 litres; the operating temperature is 70° C (158° F).

Emulsifiers [1] are added during the polymerization in order to stabilize the emulsions; H_2O_2 and potassium persulphate are used as accelerators. Modifiers serve to suppress 1 : 2 polymerization (see pg. 6); copolymerization has the same advantage. Regulators are necessary for controlling the reaction so that a maximum number of molecules with chains of an average determined length are finally obtained.

A typical recipe for making GRS is as follows:

Butadiene	75.0	parts by weight
Styrene	25.0	
Soap (solid)	5.0	
Modifier	0.5	
Catalyst	0.3	
Stabilizer [2]	1.6	
Water	180.0	
	287.4	

The reaction starts at 50 °C (120 °F) and the polymerization is about 80 per cent complete in 13 hours.

The hydrogen ion concentration is exactly regulated by means of buffering salts. After the polymerisation, β-naphthylamine is added as an anti-oxidant and many batches of the latex are blended for uniformity.

In order to obtain the rubber in a flocculent state (which is preferable with regard to the further operations) the latex is mixed at 40° C (104° F) with 12—15% of brine and then coagulated with H_2SO_4 or with alum. The

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[1] Stearin soap or soap from fish oils and from resins.
   Added at the end of the polymerization.

flocculent crumb (Fig. 90) enables an easy and quick removal of the adhering water on vibrating sieves or on rotating vacuum-filters. Then the rubber is slightly compressed into a sheet between calenders and dried either for $2^1/_2$ hrs at low temperature, or for 10 minutes at 95° C (203° F). The final operation is compressing the material into blocks of 40 to 50 lb. and packing them in paper bags.

Fig. 91. Presents a flow sheet for the manufacturing of GRS.
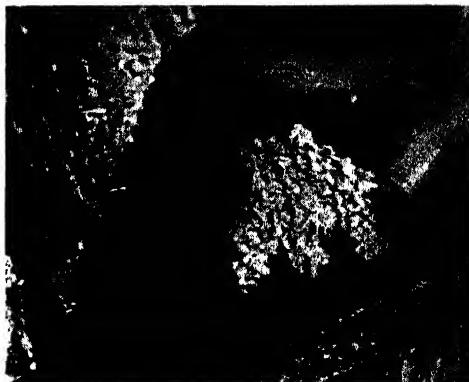
Fig. 90. Coagulated crumb of G R S.
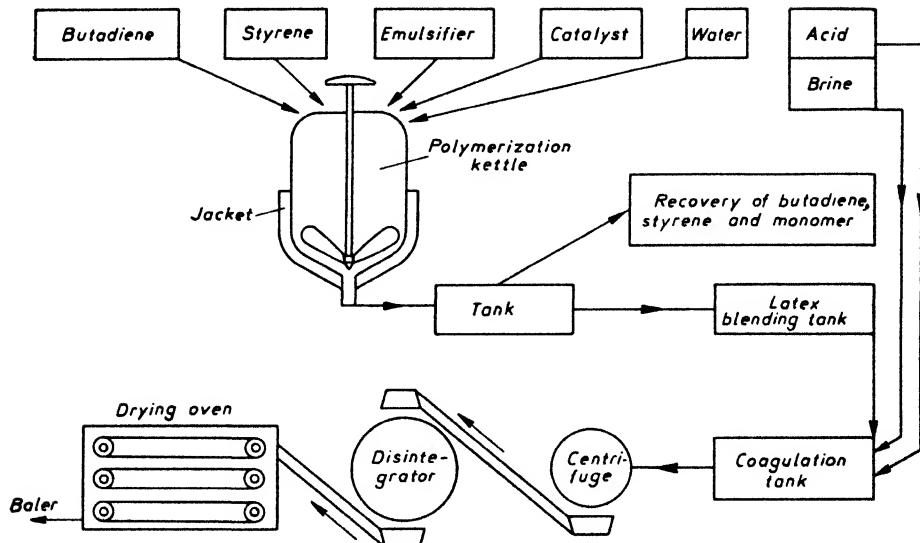
Fig. 91. Flow sheet for the manufacture of G R S.

In Fig. 92 a birdeye's view of a G R S plant is shown. The tanks for storage of the liquids and gasses are located at the banks of the river. The plant consists of independently operating units separated from each other because of the danger of fire.

On the rolls, the G R S is first masticated and then the compounding ingredients, etc. are added in a way similar to that when starting from the natural product.

Table 31 shows a typical mixture in use for treads of tyres.
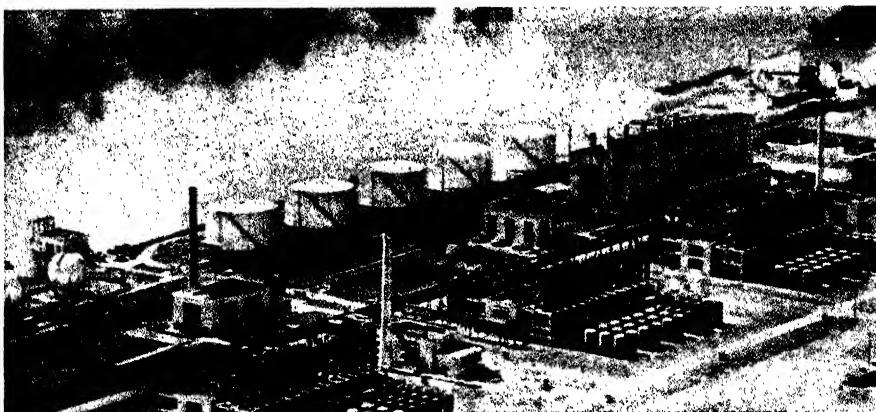
Fig. 92. View of a G R S plant.

TABLE 31.

TREAD MIXTURE FOR G R S.
(Vulcanization 30 min at 142° C (289° F)

Ingredient	Amount in g.	Purpose
G R S	100	
Paraffin, etc.	10	softener
ZnO	10 ⎱	activators for
Stearic acid	2 ⎰	vulcanization
Mercapto-benzothiazole	1.4 ⎱	accelerators
Diphenylguanidine	0.3 ⎰	
Carbon black	40	reinforcing compounding ingredient
Sulphur	3	vulcanizer
Phenyl-naphthylamine	1	antioxidant

Recently a process has been developed in which the compounding ingredient, carbon black, is brought into suspension, which is then added to the synthetic latex. Both can be coagulated; in this way the compounding room of the rubber factory can be kept clean. It is found in the literature that rubber compounded this way has superior properties.[1] The cause of this is not clear because the rubber molecules are tightly enveloped in the latex particles, so that no intimate mixing with these molecules can be expected as long as the carbon black particles are not in a position to penetrate into the latex globules.

The interlinking, discussed on pg. 14, is one of the main defects of synthetic rubbers; it leads to great difficulties in the manufacturing of articles. The molecular structure is represented in Fig. 93. This phenomenon reminds us of the experience with natural rubber, where an extremely slight vulcani-

[1] W. McMahon and A. R. Kemp, Ind. Eng. Chem., 36 (1944) 735.

$$\begin{array}{cccccccccc} H_2 & H & H & H_2 & H_2 & H & H_2 & H_2 & H \\ -C-C & =C-C-C-C-C-C-C- \end{array}$$
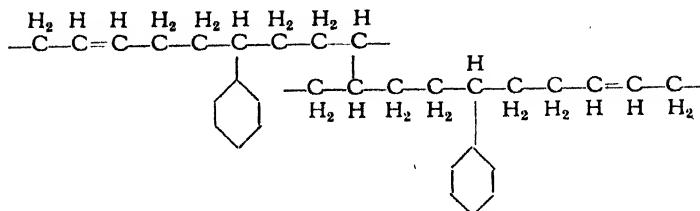
Fig. 93. The interlinking of G R S.

zation (interlinking) is quite sufficient to render almost impossible the masticating, the tubing, and the calendering operations.

This interlinking is also one[1] of the causes of the lack of tackiness, the great obstacle encountered in building up tyre bodies, transportation belts, etc.

The other great defect of most synthetic rubbers (see page 13) is the building up of irregular chainmolecules with an insufficient crystallizing capacity on stretching (see page 137).

We will enter in somewhat more detail into this question with respect to GRS, because it is of paramount importance for the synthetic rubber industry. In ordinary butadiene polymerization only about 25 per cent of the 1:2 polymer is formed.

There appear[2] to exist 8 combinations, two of which have the greatest reaction rate, see Table 32.

TABLE 32.

COMPLICATIONS DUE TO 1:2 AND 1:4 ADDITIONS

Monomer	Can react with:	Rate
1:4	1:4 and 1:2	
1:4	Styrene	high
1:2	1:4 and 1:2	
1:2	Styrene	
S	1:4 (not 1:2)	high
S	Styrene	

These two reactions, therefore, take place faster than the others; consequently the composition of the reaction mixture changes gradually (see Fig. 16, page 15.) This is the reason why the polymer is stripped after 70% conversion. Low temperature polymerization has proved to lead to more regular chains than the ordinary process at 50° C (120° F). It was shown[3] that butadiene, polymerized at 30° C (86° F), showed no evidence of crystallization when cooled unstretched to —70° C (—94° F), in contrast

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[1] Together with the branching, mentioned on page 14.

[2] Private communication.

[3] K. E. Beu et. al., J. Polymer Sci., 3 (1948) 465.

to butadiene, polymerized at 20° C (68° F) and below. Under the name Ultipara a low temperature polymerized GRS is now being put on the market, but its crystallizing capacity is still poor compared with natural rubber, resulting in inferior properties in mixtures without cboan black.

An advantage of neoprene is that because of the polarity of its monomer these complications do not arise.

One might suggest that the lack of strenght of GRS is due to an insufficient chain-length, instead of to a lack of crystallizing capacity. It was however shown[1], that already at a molecular weight of 500,000 the maximum of strength, elongation at rupture and modulus of GRS is attained, so that the formation of longer chains would be of no value[2].

The trouble due to a lack of tackiness has been partly overcome by covering the calendered sheets with natural rubber, but it still forms one of the greatest difficulties in applying synthetic rubber.

The phenomenon reminds us of the much feared scorching, encountered when masticating natural rubber containing an ultra-accelerator.

The Germans have tried to solve this problem by a thermal degradation.[3] To this end, the polymerized Buna is heated in an air oven (see Fig. 94) prior to the mixing process. The degradation is an oxidation in which the macromolecules are broken down. During the heating, however, a reverse process also occurs, namely, an interlinking of the molecules by cyclization. In Fig. 95 the curves for 115° C (239° F) and 125° C (257° F) show the correct course the process must take, because at 135° C (275° F) the interlinking takes place.
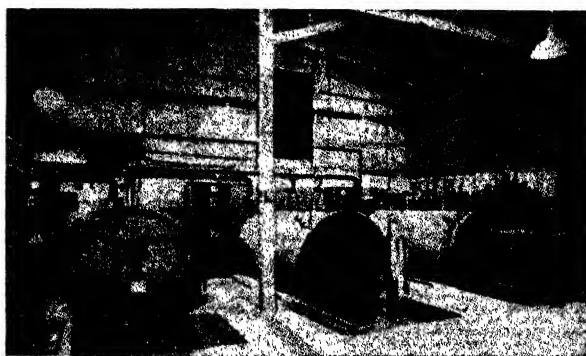
Fig. 94. Degradation oven for Buna S.

[1] J. A. YANKO. J. Polymer Sci., 3 (1948) 576.
[2] See for theoretical considerations, regarding the strength of rubber: G. GEE, *Rubber Chem. and Technol.*, 21 (1948) 301.
[3] H. HAGEN, *Kautschuk*, 14 (1938) 205.

If the heating at this temperature lasts longer than 80 minutes, the hardness starts increasing again, showing that the interlinking effect prevails over the degradation.

Although, according to the Germans, this thermal decomposition process has brought a real improvement in the manufacturing of Buna, it has not become popular in the U.S.A. All in all, an important disadvantage still exists in comparison with natural rubber. This is augmented because, on storing, the degraded Buna recommences to harden by itself. A sample which was degraded from a Defo[1] hardness 7000 to 500, hardened itself again to 800 in one week.

Notwithstanding the important difficulties, G R S can be calendered, tubed, frictioned, sprayed, and vulcanized in the same machines as natural rubber, although these operations are mostly more difficult. The vulcanization takes place at a temperature of from 110 to 150° C (230 to 302° F) and lasts 10 to 80 minutes, depending upon the wall-thickness and mixture. These circumstances correspond approximately to those for the normal practice with natural rubber.
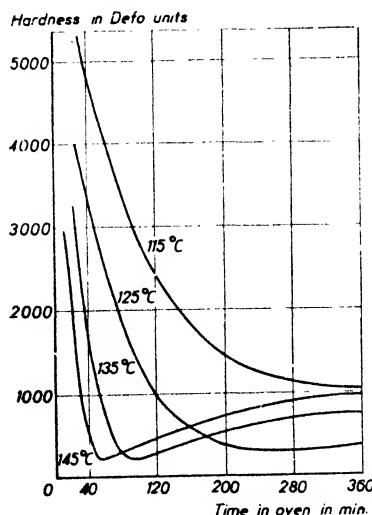
Fig. 95. During the thermal decomposition of Buna S a depolymerization (decrease of hardness) takes place first, but later on an interlinking (increase of hardness) occurs.

From G R S, *ebonite* can be made by vulcanizing with about 45% of sulphur. These ebonites are in some respects superior to those made of natural rubber in that they are more resistant to heat and to water.

Buna SS contains double the quantity of styrene. We refer to Fig. 46a (page 59) regarding the influence of the styrene content on certain physical properties. Buna SS is less difficult to manufacture, presumably because the number of double bonds is smaller, so that fewer possibilities for interlinking exist.

G R A (*German: Perbunan*) is a copolymer of butadiene and acrylonitrile, with a content of roughly 27% of acrylonitrile by weight.

$$—CH_2—CH=CH—CH_2—\overbrace{CH_2—CH}^{\text{acrylonitrile}}—CH_2—CH=CH—CH_2—$$

$$\underbrace{}_{\text{butadiene radical}} \quad \underset{\displaystyle CN}{|} \quad \underbrace{}_{\text{butadiene radical}}$$

G R A
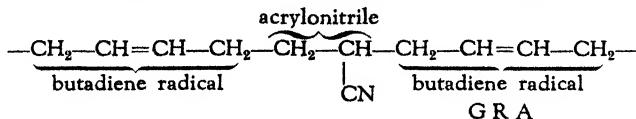
[1] The Defo hardness measures the weight in grams necessary to compress a cylinder of 10 × 10 mm in 30 sec from 10 to 4 mm. This is the standardized German method for measuring the hardness of rubbers.

To complete the range of polymers, a material with 35% acrylonitrile has been put on the market. The reason is to further improve the oil resistance (see page 143).

Neoprene (polychloroprene) is produced by first adding two molecules of acetylene, together forming vinyl acetylene. This is led through reaction tubes in the presence of HCl and a catalyst, giving monochloroprene. This is emulsified and polymerized in a reactor. As with G R S the polymerization is only carried out to a certain extent and then the unreacted monomer is removed by distillation.

A small amount of stabilizing material, such as tetramethylthiuram disulphide or phenyl-*β*-naphthylamine, is added to prevent further polymerization; moreover, softeners are also added.

The polymer is separated from the emulsion by freezing it out on a rotating drum. From this, the neoprene is scraped off as a thin film, which is dried further and folded together; Fig. 96 shows this last step of the process.
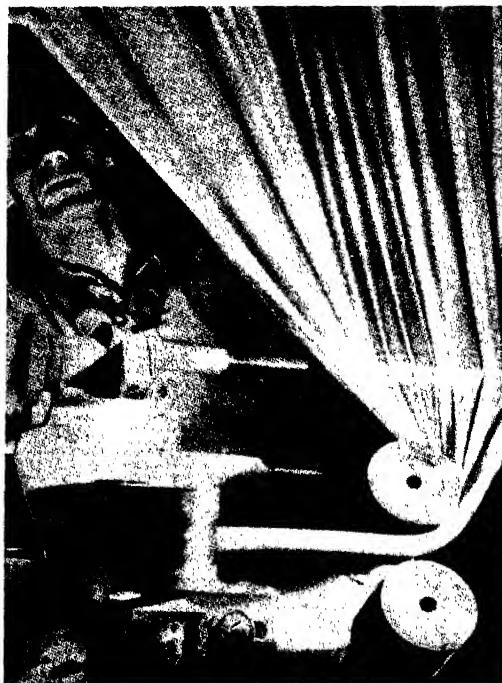
Fig. 96. Neoprene leaves the freezing drum as a thin film and is folded together into a "rod".

Neoprene is rather hard in comparison with natural rubber, but in consequence of a greater heat sensitivity it softens on the rolls at 60° C (140° F)

so that it can be compounded more easily than G R S. Unlike natural rubber and G R S, no sulphur is required for the vulcanization; in Table 33 a typical compound with outstanding heat resistance is mentioned. When heated in the press, polymerization takes place only by interlinking. This may perhaps be attributed to the ready activity of the chlorine at the tertiary C-atom which reacts easily with H-atoms. The usual vulcanization time is 60 minutes at a temperature of 140° C (284° F).

TABLE 33.

NEOPRENE MIXTURE WITH GREAT HEAT RESISTANCE

neoprene	100	g
MgO	4	,,
wood rosin	10	,,
phenyl - naphthylamine	2	,,
phenolic antioxidant	2	,,
ZnO	15—20	,,

Thiokol is obtained from ethylene dichloride on treatment with sodium and aqueous polysulphide solution during a few hours. The latex obtained is coagulated by acids, and the coagulum is washed and calendered to form a sheet. The formula is mentioned [1] on p. 23; other formulae have also been proposed (see Table 30 page 124). It is remarkable that the sulphur content is about 80%, so that one can almost speak here of an inorganic rubber. The *thioplasts*, as they are sometimes called, are vulcanizable, but, as in the case of neoprene, it is not necessary to add sulphur. In order to improve the properties, natural rubber is added. The pungent odour is a disadvantage. Thioplasts are also obtainable on the market as prevulcanized moulding powders, which are formed at a moulding temperature of about 150° C (300° F) under a pressure of 50 kg/cm² (700 p s i).

Polyisobutylene is a rubber, that cannot be vulcanized because the molecule does not contain double bonds. Therefore, it is a thermoplast, and the manufacture consists merely in a mixing and a moulding process. In order to attain rubbery properties, the molecular weight must be at least 100,000 to 200,000 To make it vulcanizable, copolymers with isoprene are produced, introducing in this way the necessary double bonds. The so-called *butyl-rubber* G R I (Government Rubber, Isobutylene type) contains from 2 to 5 per cent of isoprene.

The polymerization is not carried out in emulsion, but in solution at very low temperature (—100° C = —150° F). For this purpose, the two monomers

[1] J. C. Patrick, *Trans. Faraday Soc.*, 32 (1936) 347.

are dissolved together in methyl chloride. The catalyst is also dissolved in methyl chloride and both solutions are mixed in a container with cooling by means of liquid ethylene. The reaction takes place instantaneously and at the same time coagulation occurs so that a coagulated suspension leaves the reactor. The water is separated and the crumbs are dried and passed through an extruder.

§ 39. PROPERTIES OF THE FINISHED PRODUCTS

Generally speaking, every kind of synthetic rubber — as compared with the natural product — distinguishes itself by certain special properties. Most comparable with it is G R S, the synthetic rubber for general purposes as it is called. The others, the special kinds, differ more because characteristic groups have been introduced into the molecule in order to meet special technical requirements. Usually they are more expensive (see p. 247) and so they only justify themselves in cases in which their special properties can be used. We shall therefore review these cases in particular.

A general comparison is made in Fig. 97 between the stress-elongation curves of the most important kinds of synthetic rubbers and of natural rubber. From this study it appears that, provided the degree of vulcanization and the proportion of the filling materials are chosen properly, one obtains for natural rubbers and for vulcanizable synthetic rubbers of good quality (GRS, GRN, Neoprene) an almost identical course of the curves. This alone, however,
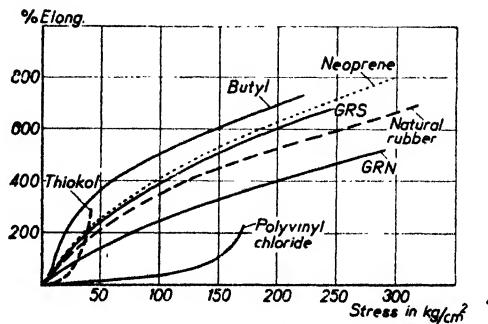
Fig. 97. Stress-elongation diagrams of the most important synthetic rubbers in a suitable technical mixture.

is in itself not decisive for a final evaluation, because the question is not only how a rubber behaves when stretched. Perhaps still more important is how it springs back (slowly or quickly, entirely or incompletely), how it ages, how are the wearing and the electric properties, whether it is permeable to gas, susceptible to swelling agents, etc. For a more general comparison,

we refer to Table 35 in which the special characteristics connected with these properties have been summarized.

It should be expressly mentioned that — except for the electric properties — in most cases, mixtures filled only with carbon black are compared with one another; the majority of synthetic rubbers without active fillers possess few noteworthy properties. The reason for this is that these rubbers do not crystallize on stretching, so that all the possible minima of potential energy between the chains are far from being realized. Active fillers seem to fulfil a "glueing action" between the chain molecules, compensating for the lack of crystallinity.

Without this very important action of carbon black, all rubbers of the first group mentioned in Table 34 would be of no practical value. In contrast to this are the rubbers of the second group, which all crystallize and for which

TABLE 34.

REINFORCING EFFECT OF CARBON BLACK ON VARIOUS RUBBERS [1]

Rubber	Tensile strength (kg/cm²)		Tensile rein-forcing effect of carbon black
	unloaded vulcanizate	loaded vulcanizate	
First group (non crystallizing):			
Polybutadiene (Na)	15—25	120—180	5 to 12 times
GRS	20—30	150—200	5 to 10 ,,
GRA	20—40	150—200	4 to 10 ,,
Polyisoprene	15—20	100—150	5 to 10 ,,
Polymethylbutadiene	20	80—120	4 to 6 ,,
Second group (crystallizing):			
Natural rubber	200—300	300—325	1 to 1.6 ,,
Neoprene	150—200	200—250	1 to 1.7 ,,
Polyisobutylene (butyl rubber)	250—350	300—350	1 to 1.4 ,,

the effect of carbon black is only of minor importance. Extremely interesting is the comparison between polyisoprene (first group) and natural rubber (second group). Here, the great regularity of the chain molecules formed in nature and leading to a ready crystallization on stretching shows its great technical advantages compared with the irregular chains formed in technoolgy (compare page 13 for the sources of these irregularities).

The natural rubber of Table 35 has been vulcanized in a so-called sulphur-free mixture.[2] For the sake of completeness the non-vulcanizable rubbers: polyisobutylene and polyvinyl chloride (see page 116) are likewise included, although

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[1] A. P. ALEXANDROV and J. S. LAZURKIN, *Rubber Chem. and Technol.*, 19 (1946) 42.

[2] Namely with tetramethyl-thiuram disulphide as a vulcanizer. This splits off sulphur which combines with rubber. In this manner, care can be taken that, with a possibly low content of bound sulphur, optimal properties are obtained. In modern rubber technology this is the right method for manufacturing products with good mechanical and ageing properties.

TABLE 35.

Comparison of the most important properties of synthetic rubbers with those of natural rubber

(Mixtures contain carbon black, unless stated otherwise)

No.	Mixture	Tensile strength [1] kg/cm² psi	Elongation at rupture %	Tear resistance kg/cm² psi	Permanent set after 24 hours at 200 % elongation %	Ageing time for 25 % decrease of strength in air of 70° C (GEER-EVANS) weeks	Dielectric loss factor tg δ (at 800 Hz[2]) 10⁻⁴	Oil resistance petrol and oil	Oil resistance ben-zene	No.
	A. Vulcanizable									
1	Natural rubber. Vol % carbon black = 25 . . .	310/4400	600	200/2900	10	25	30	d	d	1
2	G R S [5], Vol % carbon black = 30	230/3200	550	55/800	10	15	50	r	d	2
3	G R A [6], Vol % carbon black = 30	290/4100	600	55/800	10	20	450	r	d	3
4	Neoprene G. Vol % carbon = 20	275/3900	750	180/2600	6	20	>300 [4])	r	d	4
5	G R I (Butyl rubber). 30 % carbon black . . .	200/2800	800	—	6	25	—	d	m	5
6	Thiokol. Vol % carbon black = 35	45/650	250	40/570	—[3])	>8	—	r	m	6
	B. Non-vulcanizable									
7	Polyisobutylene .	50/700	1000	—	90	—	—	d	r	7
8	Polyvinyl chloride with plasticizer	180/2500	220	150/2100	>100	good	1000 at 50 Hz	d	d	8
	C. Minimum values for average technical purposes	125/1750	300	—	max. 20	—	—	—	—	

□ indicates: essentially better than for natural rubber.

▨ means: essentially worse than for natural rubber.

r = resistant m = medium d = dissolves

[1] Measured on 1 mm test pieces.
[2] Mixtures without carbon black and with good insulating fillers (talc, etc).
[3] The permanent set is 6% at 75% elongation.
[4] For Neoprene E.
[5] The mechanical properties of Buna S are somewhat better.
[6] For the corresponding Perbunan mixtures, the strength is somewhat greater.

from a technical point of view we can hardly regard them as being rubbers. To prove this, we point to the unfavourable permanent set, which in the case of experiments of longer duration would turn out even more unfavourably. In the table, the values which are essentially better than those for natural rubber are indicated by [   ] , whereas the values which are worse are marked ┊............... .

The table should be read as follows. The tensile strength and the elongation at rupture indicate average values attainable when the material under consideration is judiciously vulcanized. The figures for the first four kinds show that for these an approximately comparable state can be attained. This also appears from Figure 97. It is also evident from these two columns that thiokol and polyisobutylene, from a general mechanical viewpoint, do not satisfy high requirements. The combination of 125 kg/cm² (1750 psi) tensile strength and 300% elongation at rupture are recognized as minimum values for general technical purposes. For high-class articles the requirements lie much higher [1], namely at 200 kg/cm² (2800 psi) and 450%.

GRS is apparently on an approximately equal level with natural rubber. The resistance against tear is lower, which may be connected with the poor crystallization capacity. This low tear resistance would lead to the expectation that the abrasion properties would also be worse. In practice, however, there is no very great difference in this respect. Another phenomenon, which is presumably connected with the lack of crystallization, is the so-called cut growth. This means that on repeated bending an incision starts to grow rapidly, leading to the well-known surface cracks in tyres. The most serious defect of G R S, however, is the heat development in tyres due to the considerable hysteresis losses. This is the reason that large tyres are still subject to a certain speed limit. It is doubtful whether this defect can be improved, the heat development probably being connected with the polarizability of the benzene groups. In mixtures without carbon black, the absence of crystallization due to an irregular chain structure makes GRS of very little value.

GRA belongs to the special rubbers. It offers the great advantage of possessing a greater resistance to petrol and oil than natural rubber; this becomes more pronounced the higher the content of acrylonitrile. On the other hand, there are the disadvantages of the lower impact resistance, the inferior electric properties, slower recovery after deformation (although this does not find expression in Table 35), and the higher price.

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[1] For good hoses, 100 kg/cm² (1420 p s i) and 300% elongation is desired; for conveyer band surfaces, 200 kg/cm² (2840 p s i) and 45C% elongation. In Table 35 all values have been determined with test pieces of only 1 mm, but the requirements for hoses, etc., are based on thicker pieces (3—5 mm), leading to 20—30% lower values.

Neoprene[1] at first sight seems to have wider possibilities than GRS, not only with respect to the resistance to oil but also for the tear resistance — both being good. However, it has proved itself not to be suitable for tyres and for electrical purposes owing to the presence of the polar Cl-atom which leads to a considerable development of heat (hysteresis; tg δ). Moreover, it is one of the most expensive kinds of synthetic rubbers.

Butyl rubber, the copolymer of butadiene with 5 or 10% of isoprene, has a stress-strain curve[2] which is rather different from that of natural rubber. Nevertheless, it is a useful material and its extremely low permeability to gases has led to its application in inner tubes. Its elastic properties are very peculiar because it hardly rebounds at room temperature, whereas at 100° C it closely resembles natural rubber in this respect. Due to the fact, that polar groups are practically absent, Butyl rubber has very good electrical properties. Its vulcanization rate is small as a consequence of the limited number of double bonds. This also makes it understandable that the ageing properties are superior to those of natural rubber.

Low molecular polyisobutylene is added to lubricating oils in amounts of 1 to 2% in order to reduce the sensitivity of the viscosity to temperature.

Thiokol as a representative of the *polyethylene polysulphide* series is —as stated already — a material which, from the point of view of the rubber technologist, is inferior. So many properties are inferior compared with those of natural rubber (tensile strength, elongation at rupture, cut growth, time-influence on the mechanical properties), that applications can be found only in cases where these defects play no part, and where on the other hand the specific good properties (oil resistance) can be made use of.

We may mention electrical insulators for cases in which no high requirements exist, and gaskets for purposes in which the material comes into contact with oils.

Polyvinyl chloride, when plasticized with a very large amount of plasticizer (up to 100%) also shows rubbery properties — as has already been discussed above. Its resistance to oxidation compensates for the 2 to 3 times higher price compared with natural rubber, but this limits the applications to large surfaces. The ideal method of use is as a coating on a textile underlayer, since then the poor mechanical properties are compensated by the strength of the textile fibres.

Polyethylene shows, to a certain extent, rubbery properties when it is not too completely crystallized (see page 108). It is non-vulcanizable, as it possesses no double bonds.

[1] See for the properties D. F. FRASER and N. L. CATTON, *The Neoprenes,* Dupont Report., 1942.
[2] R. M. MOORE et al., *Ind. Eng. Chem.,* 32 (1940) 1283.

Polyvinyl butyral can also show rubbery properties. For a discussion of these "vulcanizable" materials see page 121.

Foɪ *silicone rubber* the reader is referred to page 237.

As regards the *ageing properties* of rubbers in Table 35, we would point out that, in the literature, data are often found differing from the values given, and which for natural rubber show inferior quality. Such are the cases mentioned already (note 2, p. 137) in which the vulcanization took place with a too high sulphur content or without an antioxidant. In our opinion such comparisons are inadmissible. To prove this, we may refer to Fig. 98, in which the decline of strength and elongation during the artificial ageing in the Geer-oven (see page 80) is represented [1] for the most important rubbers. Although small differences exist occasionally, no great differences appear.

a) Decrease of tensile strength.   b) Decrease of elongation at rupture.
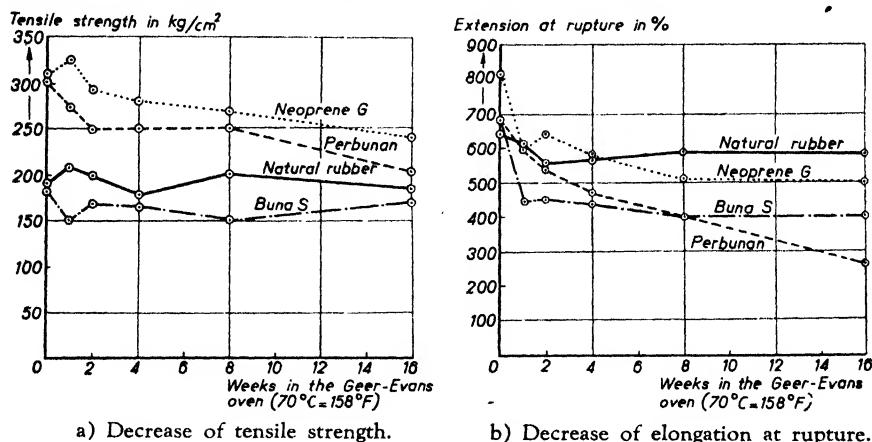
Fig. 98. In the accelerated ageing test [according to Geer-Evans in air at 70° C (158° F)] synthetic rubbers of good quality behave approximately in the same manner as modern natural rubber mixtures.

GRA shows a rapid decrease in elongation at rupture, which is not found for the tensile strength, so that as a whole this material cannot be regarded as showing worse ageing properties than the other rubbers. The experienced rubber investigator knows how to evaluate the results of this kind of research.

A few words should be said particularly about the *resistance to swelling*. One usually speaks of the oil resistance, for it is especially the need of an oil- and petrol-proof rubber (which is met by GRA, Neoprene and Thiokol). That this improvement of the swelling resistance is due to a specific action and does not apply to any liquid may be proved by the following figures:

[1] A. . Wildschut, *Technol. Invest. on Natural and Synthetic Rubbers*, Amsterdam 1946.

TABLE 36.

SWELLING BEHAVIOUR OF SOME KINDS OF RUBBER IN VARIOUS FLUIDS [1]

Kind of rubber (vulcanized)	Swelling in volume %, after 8 weeks at 20° C (68° F)			
	Diesel oil	Benzene	Ethyl alcohol	Ethylene chloride
Natural rubber	116	360	2	125
G R S (Buna S)	75	285	1	150
Buna S S	60	290	1	—
G R A (perbunan)	13	210	10	240
Perbunan extra	5	125	10	—
Thiokol	3	190	4	> 500

Especially interesting is the action of ethyl alcohol and ethylene dichloride as shown in Table 36. It is the polar rubbers GRA and Thiokol which are the least resistant to these polar liquids. To explain this, we refer to Fig. 39 (p. 52). Supposing that the groups indicated therein by K_1 represent the polar CN-groups of the GRA, one can imagine that these are not separated from one another by non-polar solvents like petrol or benzene, because they do not enter between the K_1-groups. In a partially polar liquid such as ethylene chloride, however, the polar parts will separate the K_1-groups from each other and the non-polar parts the K_2-groups.
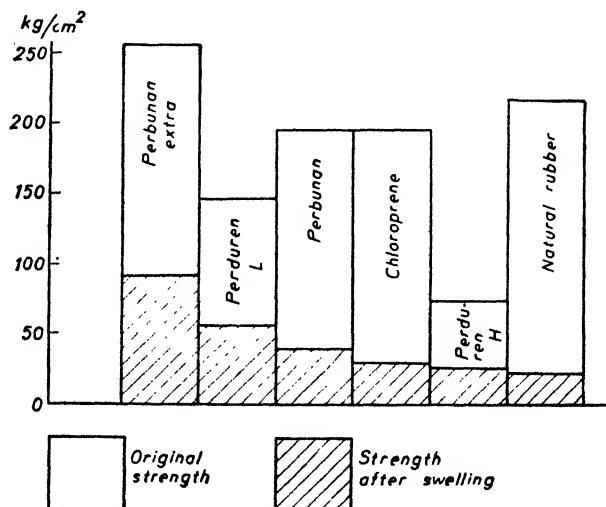
Fig. 99. Tensile strength after swelling for 8 weeks in turpentine at 20° C [2]

[1] Partly from the author's own investigations, partly borrowed from F. S. Rostler and R. M. White, Rubber Age (N.Y.), 61 (1947) 313.
[2] H. Barron. Modern Synthetic Rubbers, London 1945, p. 210.

The strength in the swollen condition is perhaps still more important for technical purposes. In Fig. 99, data with regard to this feature is given, showing that in the swollen condition there is no spectacular difference in strength between the various rubbers.

The *permeability to gas* is a property especially important for inner tubes and for balloons. As appears from Table 37, it differs greatly for the various kinds of rubbers and also for the type of gas under consideration.

TABLE 37.

PERMEABILITY TO GASES [1] OF DIFFERENT KINDS OF RUBBER
IN 10^{-8} cm^3 PER SECOND PER cm^2 FOR A THICKNESS of 1 cm (1 ATM, 25° C (77° F))

Kind of rubber	H$_2$	O$_2$	N$_2$	CO$_2$	He
Natural rubber (vulc.)	40	18	7	102	23
G R S ,,	31	13	5	94	18
G R A ,,	12	3	1	23	9
Neoprene G ,,	10	3	1	20	—
Thiokol B ,,	1	0.2	—	2	—
Ebonite ,,	0.3	—	0.005	—	0.8
Butyl rubber ,,	4	—	0.3	—	5
Vistanex (polyisobutylene)	5	0.9	0.2	4	6
Koroseal (polyvinyl chloride)	8	—	—	—	—
Pliofilm (HCl-rubber)	1	—	—	—	—
Polyethylene	1	—	—	—	—

On p. 49 the importance of the *brittle* point was pointed out, which for rubbers measures that temperature at which the material changes from the rubbery high-elastic into the hard and brittle state.

It appears from Table 38 that introducing polar groups raises the brittle point, as is to be expected from the increase in secondary coherence. Hence,

TABLE 38.

BRITTLE POINT T$_b$ OF SOME RUBBERS [1]

	T$_b$	
	°C	°F
Natural rubber (raw or soft vulc.)	—58	—72
Polyisobutylene	—50	—58
Polyvinyl chloride (plast. 40% dibutyl phthalate)	—46	—52
Butadiene acrylonitrile	—44	—48
Neoprene G N	—40	—40
Thiokol F	—35	—31
G R S (35% styrene)	—33	—28
Polystyrene	+80	+176
Polyvinyl chloride	+81	+178

[1] G. J. van Amerongen, *Thesis*, Delft 1943; T. P. Sager, *J. Research Nat. Bur. Standards*, 25 (1940) 309.
[1] Figures from R. F. Boyer and R. S. Spencer. *Advances in Colloid Science*, New York 1946, p. 33.

the best rubbers with regard to cold resistance are natural rubber and polyiso-butylene. It is interesting to note how important the action of a plasticizer may be, a point already discussed more quantitatively on page 57.

In the emulsion polymerization the synthetic rubbers are obtained in the form of *latex* and it is practical to utilize them as such. Nowadays, synthetic latex is used for the manufacturing of artificial leather, for artificial cork, for sealing purposes and also for the impregnating and coating of tissues. In many cases, however (vinyl chloride), no completely closed film is formed. It may be that the protective colloids form a cohering network throughout the film, leaving canals for moisture to penetrate. For this reason, it is advisable to press such coated surfaces under hot conditions because there seems to be a fusing action. A great disadvantage of most synthetic latices is that carbon black cannot be brought into the interior of the latex globules so that no close contact between the polymer molecules and the black can be effected. Since such an intimate contact is indispensable for many synthetic rubbers for obtaining good mechanical properties (see above), the products obtained from these latices have poor properties. For this reason, GRS latex is usually mixed with natural rubber latex.

CHAPTER VIII

POLYMERS BASED ON PHENOL AND ANILINE

§ 40. RAW MATERIALS

As raw materials for the phenol and cresol resins, which among others under the historical name of "bakelite" have gained great importance, the raw materials shown in Fig. 100 are important. With the exception of aniline these are usually designated as "phenols".

	Phenol	m-Cresol	p-Cresol	Aniline
Boiling point:	182°C.	202.8°C.	202.5°C.	182°C.
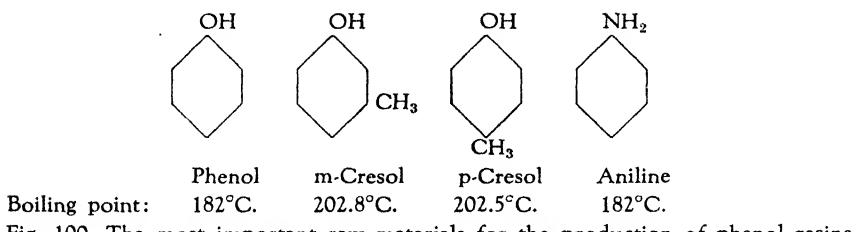
Fig. 100. The most important raw materials for the production of phenol resins.

These are all obtained directly from coal tar or coke oven tar but a great quantity of phenol is also manufactured synthetically from benzene [2]. In particular, the so-called medium oil fraction of the tars, boiling between 180 and 250° C (356 and 482 °F), is very rich in *phenol* and *cresol*. This fraction is subjected to a second distillation, during which a concentration of the phenols, cresols, and naphthalene takes place. The latter product is separated by cooling. The phenol is converted by NaOH into Na phenolate, which is soluble in water and can be removed. The o-cresol is removed by distillation from the remaining mixture of isomeric cresols. m- and p-cresol are not easily separated, so that their mixtures are used for the manufacturing of resins. As the m-cresol furnishes the most quickly hardening resins, the commercial value of the mixture depends on its content of m-cresol. In the market there are two main mixtures, the better one with 60 to 65%, the cheaper one with 40 to 45% m-cresol.

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[1] See for an extensive treatment: T. S. CARSWELL, *Phenoplasts*, New York 1947.
[2] According to the RASCHIG method, air and HCl together with benzene vapour are conducted over a contact substance. The chlorinated benzene formed is converted with the aid of steam into phenol and HCl.

In practice, the mixtures generally also contain some xylenols and part of them harden very quickly, part of them very slowly [1]. Considering the great number of possible variations, it is understandable that it is always difficult to furnish cresols with exactly the same reaction rate.

Aniline is found in tar in smaller quantities only; it can be made by reduction of nitrobenzene. The other important raw materials for the manufacturing of phenol resins are the aldehydes:

Formaldehyde   Furfurol
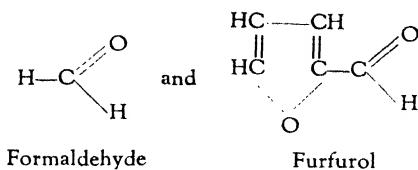
Formaldehyde is manufactured by oxidation of methyl alcohol or by reduction of CO by water-gas under high pressure. Furfurol which is sometimes used instead of formaldehyde, is manufactured from corn-cobs, oat-straw, or by the saccharification of wood.

The *fillers* [2] used in moulding powders are as important as the resins themselves; most widely used is wood flour made from soft woods like pine, Norway fir or spruce. The fineness is usually between 60 to 100 mesh (usually 80 mesh). For the shock-proof compounds, short cotton fibres, fabric cuttings and pulp flakes, or chopped paper are used. Sisal fibre is used in special cases where a mediocre surface finish can be used (technical articles). The cause of the beneficial effect of the coarse fillers was (page 40) shown to be due to their damping effect on mechanical shock waves. The heat-resistant materials require inorganic fibres like asbestos floats and ground slate. If a combination of heat-resistance and great mechanical strength is necessary, asbestos cord and glass fabric can be used. We shall see further on that the mouldability becomes worse the coarser the compounding ingredient, so that there is a certain limit.

As further ingredients we mention metallic oxides like MgO, which prevent the surfaces of the moulds from becoming dirty. Stearin, stearates, and oils are also added as plasticizers, hexamethylene tetramine as a source of formaldehyde and ammonia (p. 153) and moreover organic or inorganic dye-stuffs.

[1] The reactivities of 10 different components in tar have been investigated by H. von Euler,
     Angew. Chem., **54** (1941) 458.
     See for a critical review: L. Debing, *Modern Plastics* **25** (1947) 127.

§ 41. MANUFACTURING PROCESS OF RESINS AND MOULDING COMPOUNDS

The manufacturing process of the phenol-formaldehyde products which is represented schematically in Fig. 101, consists essentially of three steps, the manufacturing of the resin, the manufacturing of the moulding compound and the moulding process proper.
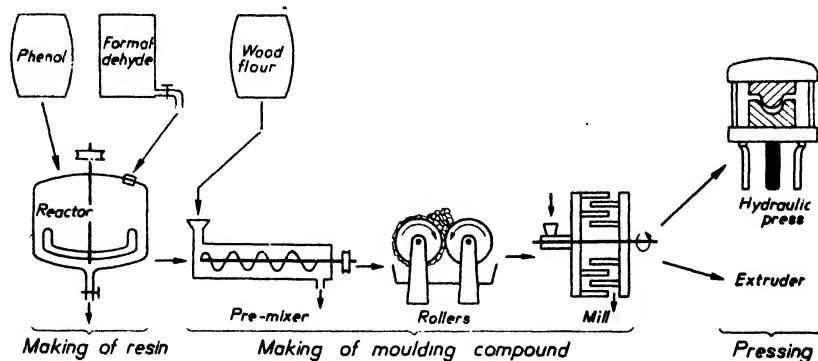
Fig. 101. Flow sheet for phenol-formaldehyde products.

a. Resins.

On page 2 we mentioned briefly the reaction of phenol with formaldehyde as an example of a condensation and in Fig. 53 we represented the product
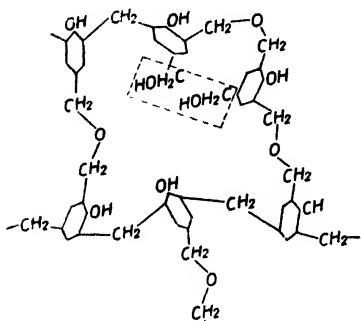
Fig. 102. Structure of a phenol formaldehyde resin.

The two CH_2OH groups, indicated by :......... are too far apart from each other to react (Lockerstelle).

which forms, taking into account the ether bridges between the phenol-nuclei, which seem to form to an important extent. The irregular grouping is responsible for the amorphous structure.

On p. 34 it was mentioned that such resins show only about 1/500 to 1/1000 of the strength calculated theoretically. This can be explained by the fact,

that — as shown in Fig. 102— the reaction does not actually take place at every spot capable of reaction. There thus remain certain chinks (Locker-stellen), see also page 34, which by their notch-effect considerably reduce the strength.

The reaction is carried out either in an alkaline or acid solution, whereby products with fundamentally different properties are formed.

In an acid solution, 1 mole of phenol (or cresol) to 0.8 mole of formaldehyde may be used and the so-called *novolacs* (Fig. 103a) are thus formed, which are fusible and on being heated do not harden further. This is advantageous because the resins can be kept plastic for a long time in this way, making the mixing with other ingredients very easy.

By adding more formaldehyde and rendering them alkaline, the resins become capable of being hardened [1] (so called two-step resins).
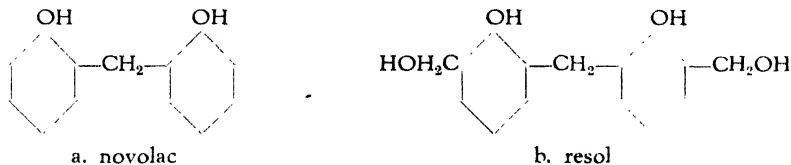
a. novolac   b. resol
Fig. 103. Initial products in the phenol-formaldehyde resinification.

In alkaline solution, one mole of phenol to 1.5 mole of formaldehyde is used, thus forming the so-called *resols* (Fig. 103b) which in the beginning are liquid, but on being heated gradually change into a solid but still fusible resol. On further heating these enter into the rubberlike, highly elastic *resitol* state and finally into the infusible *resit* state. These three phases are also designated as A, B, and C states. A-resin is soluble, B-resin is partly [2] soluble and C-resin is insoluble in alcohol. The entire change from A to C is denoted as hardening and the *hardening rate* is of the greatest technical importance because upon it depends the ultimate manufacturing tempo in the moulding shop.

The reaction rate for an ammonia catalysed mixture, which is initially equimolar with respect to phenol and formaldehyde, is given [3] by:

$$K = \frac{1}{C^{1.38}t} \log \frac{a}{a-x} \quad \ldots \ldots \ldots \ldots \ldots \ldots (24)$$

where C = catalyst conc., a = the initial formaldehyde conc., and a — x = the formaldehyde conc. at time t.

[1] See for recipes: G. M. Kline, *Brit. Plastics*, **18** (1946) 170.
[2] An extensive theory of the gelation as a function of three dimensional net-formation gives P. J. Flory, *J. Phys. Chem.*, **46** (1912) 132.
[3] B. W. Nordlander, *Oil Paint Drug Reptr.*, **130** (1936) 3, 27.

The manufacturing of the resol is carried out in an autoclave with a mechanical agitator, as shown in Fig. 104. The apparatus is provided with a heating jacket in order to supply the heat necessary for the induction of the reaction. However, when the reaction starts, so much heat is evolved that it has to be removed by means of cooling water. In the beginning a reflux condenser is used in order to prevent the escape of the reacting substances.

As soon as the resin has formed, distillation at reduced pressure (10 mm) is effected in order to remove as much as possible the last volatile products. Especially in the case of quickly hardening resins, care must be taken that the
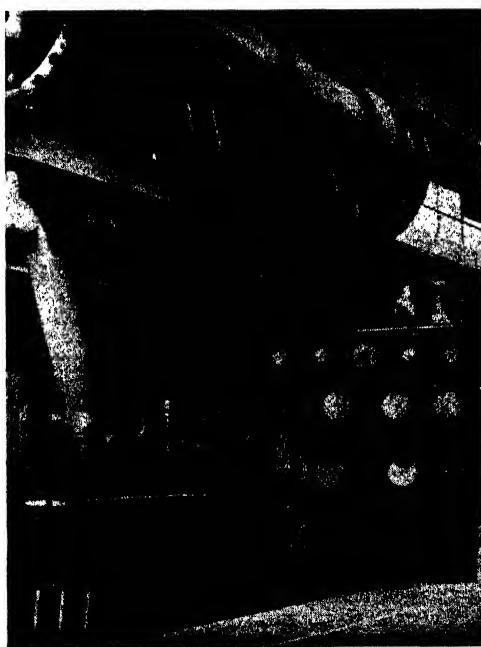
Fig. 104. Reactors for making P. F. resins (courtesy Bakelite Ltd).

reaction is interrupted at the right moment, since otherwise the resin becomes too hard and products with too high a melting point are obtained. In view of this, the melted resin is forced to flow out quickly onto flat plates which are cooled.

Now let us consider further the transition A→B→C. In the A-state the resin can be liquid or solid, but in the latter case it is still fusible. In Fig. 105 the liquid state (A_{liquid}) is represented with the majority of the particles still in free BROWNian motion. A_{solid} represents the solid resol phase. Here, it is presumed that the greater part of the particles cohere by secondary forces

so that their BROWNian motion is hindered, but the cohesion can easily be removed by heating so that the particles resume their BROWNian motion: the resol melts. On further hardening, more and more primary bonds

A liquid (resol)   A solid (resol)

B (resitol)   C (resit)

○ freely rotating units
O units, cohering by secondary bonds
● units, cohering by primary bonds
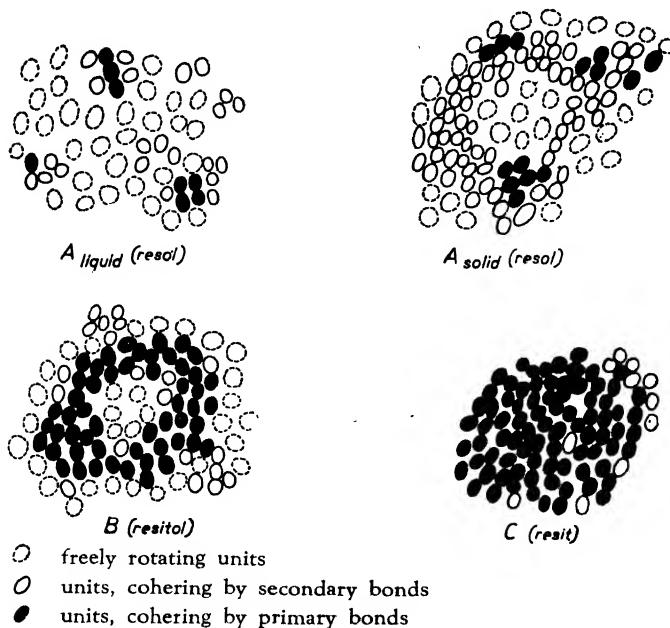
Fig. 105. Changes of structure in a three-dimensionally hardening resin.

gradually form between the particles, and C represents the final phase (resit) in which all particles are linked irreversibly, i.e., cannot be separated any more by heat or by applying force. This means that the resin can no longer be rendered plastic.

Between the A- and the C- phase lies the resitol or B-phase. Here, some of the particles, but not all, are connected by primary bonds so that a kind of network forms which on heating shows rubbery elastic properties. This can easily be observed when a resin without compounding ingredients is masticated on heated rollers. The high-elastic, rubberlike state sets in suddenly but soon changes into the hard, brittle C-stage.

The rather sharp differences in physical behaviour in the A, B and C stages makes it possible to use them for measuring the hardening velocity of a P.F. resin. For this purpose the number of seconds at 150° C necessary to bring the A resin into the C-stage is recorded [1].

R. A. BARKHUFF and T. S. CARSWELL, Ind. Eng. Chem., Ind. Ed., 36 (1944) 461.

The changes in structure during the hardening process can be followed by making thin resin films swell in acetone and examining them under the microscope with dark-field illumination. It then appears that the material is full of chinks (BARKHUFF, l.c.). These investigations support the supposition that even in the C-stage there are discrete regions interlinked with each other by only a few methylene bridges, a point which was stressed on p. 149 in relation to the fact that the strength of the final products is much lower than would be expected theoretically.

b. Moulding compounds.

The manufacture of moulding compounds from resins can be carried out in different ways, according to the type of ingredients added. If these are fine (wood floor), the mixing process on rollers is usually applied. In this process the resin, premixed with the wood flour, is brought to its melting point on the heated rollers (110° C = 230° F), thus enveloping and impregnating the compounding ingredients, see Fig. 106.

The purpose of the masticating process is to bring about a thorough mixing while at the same time, in consequence of the heating, a further condensation takes place with elimination of water. In practice, one starts from the solid A-phase, reaching on the rollers about the B-phase. Then the mass is quickly removed from the rollers and if necessary cooled, so as to stop further condensation. In the B-state it is then possible at a temperature of 150° C (302° F), this being the temperature of the mould, to make the material flow under high pressure; the transition B → C takes place in the mould within a few minutes.

A typical mixture for a wood flour compound is:

TABLE 39.

P. F. — WOOD FLOUR MIXTURE

Phenol-formaldehyde resin (novolac)	400 g
Hexamethylenetetramine	60 g
Wood flour	550 g
	1010 g

As regards mixtures containing woodflour and fine asbestos, the fibres are still sufficiently small to glide undamaged through the rollers. However, when textile cuttings are used, this becomes impossible. For such materials it is better to use kneaders (Fig. 60, p. 88) or other mixers which work more gently. In these cases, however, the resin must be used in the liquid state, either as a liquid resol or in alcoholic solution. The condensation as far as

the B-stage is then carried out in an oven after evaporating the solvents. It is impossible to carry out the condensation in the kneader because this would have to be too heavily constructed in consequence of the very high viscosity of the resin in the B-stage. Taking into account, as mentioned on p. 146, that the starting material according to its composition can have different hardening rates depending on its composition and when we further take into account that it is necessary to reach exactly a certain degree of condensation corresponding to the B-state, it becomes clear that the resinification process has to be regulated very accurately. This is rendered still more difficult, because the ingredients can vary with regard to moisture content and composition. Here lies one of the main difficulties in controlling the manufacture. Too low a condensation degree on the rollers means too long a moulding time in the moulding shop and a bad surface of the finished products; a condensation pushed too far means a bad flow capacity.

In the mastication process described, a difficulty is often encountered when starting from a quick setting resin. The hardening then proceeds so rapidly that while on the rollers too little time is available for the proper mixing process. In order to avoid this difficulty, the so-called two step process has been developed in which one starts from a novolac (p. 149) which in the first

Fig. 106. Mixing of a wood-flour compound on the rollers.

stage is melted on the rollers and mixed with the compounding ingredients. In the second stage, hexamethylene tetramine is added, from which formaldehyde and ammonia split off. In novolac, only 0.8 mole of formaldehyde per mole of phenol is present, which is insufficient to carry through the hardening as far as the C-stage. Hence the fluid state can be maintained at will on the rollers. Only by adding more formaldehyde in alkaline conditions (hexamethylene tetramine) can a thorough hardening be obtained — thus giving rise to the excellent quick-moulding compounds, manufactured nowadays.

The material leaves the rolls in the form of a sheet or, in the case of coarse fillers, in crumbs, and for the majority of purposes has to be ground. For this purpose, in the case of wood-flour mixtures, high-speed disintegrators are used.

A new type of compound has been developed, starting from long *sisal* fibres (up to 25 cm = 10 inches). These are impregnated with phenol-formaldehyde resin and blown against a screen, leading to a kind of matting. Pieces

of this matting are used in the mould. The impact resistance of the *corolite* thus obtained is about six times that of a wood flour ⹁ mixture.

§ 42. MOULDING PROCESSES

Various methods exist[1] for manufacturing finished products from the moulding compounds. The most important ones are compression moulding, extrusion, and injection moulding.

a.   Compression moulding.

The ability to flow readily in the mould is of great importance. One would therefore be inclined not to push the condensation on the rollers very far, but, on the other hand, practice has shown that easily flowing mixtures have the following four disadvantages:

1.   the baking in the mould lasts too long because we are concerned with an equilibrium reaction (see p. 7) and the lower the condensation degree of the moulding powder the more water is liberated, stopping the chemical reaction.

2.   the surface of the moulded article is unsatisfactory.

3.   the readily flowing mixtures have a tendency to adhere to the walls of the moulds.

4.   the electric properties are inferior because the finished product contains too much reaction water.

In general, the necessary compromise is shifted to the side of the stiffer compounds by using heavier presses. The pressure of 250 kg/cm² (3,500 psi) indicated sometimes in the literature is a low limit; particularly for high pieces a pressure of 400 or 500 kg/cm² (6,500 psi) is preferable. More moulding enterprises become failures on account of too low pressures being used than by the contrary. Fig. 107 shows the relation between flow and pressure. A well equipped moulding shop has a whole series of presses of from 5 tons up to 500 or 1,000 tons and in special cases even up to 10,000 tons. Depending on the size of the moulded piece, multiple moulds containing up to 50 cavities can be fixed into one press, leading to real mass production as in the injection moulding technique.
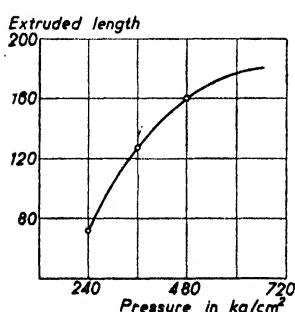
Fig. 107. Relation between flow (measured as the extruded length in a certain time) and moulding pressure.

[1] See for a practical view: D. A. DEARLE, *Plastic Moulding*, Brooklyn 1944.

Preheating the moulding compound to about 80° C (176° F) before bringing it into the mould has proved to be very useful and is being applied more

Fig. 108. Some finished products from phenol-formaldehyde moulding substances.

and more. By doing so, a uniform distribution of the temperature is guaranteed, and in this way the above-mentioned compromise can be shifted considerably in the direction of the stiffer flowing mixtures. In this respect, high frequency heating (p. 98) has brought about a considerable improvement, especially for mouldings with thick cross-sections.

Fig. 108 shows the great variety of moulded pieces which can be obtained. Nowadays one is able, owing to the development of special presses and moulds, to satisfy very rigorous requirements regarding moulding technique.
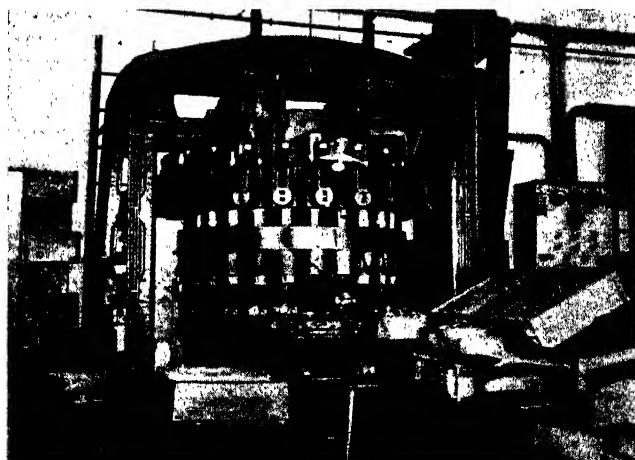
Fig. 109. Rotary moulding press.

In the moulding shops, small articles of a few grams as well as big radio-casings weighing many kilograms are manufactured. Fig. 138, p. 181, shows a close ￀ up of a hydraulic press in operation. The moulding technique has developed considerably in the direction of mass-production. Rotary moulding presses have been constructed for this purpose, see Fig. 109.

In the majority of cases the pressed pieces before being delivered require some finishing operations such as trimming, drilling, fraising, etc.; we shall not go further into these processes. In special cases, the moulded piece is subjected to a subsequent hardening in the oven in order to improve the electrical properties and the heat resistance. In this way the hardening, which is not usually completely finished in the press due to the establishment of the condensation equilibrium (page 7) is brought to a finish and all retained water-molecules are removed.

The pressing of laminated paper and fabric plates impregnated with artificial resins takes place in large multiple presses (Fig. 114, p. 161). The preparation of the material is discussed there.

A few words may be devoted to the cold moulding process although it is rather out of date. It is still used for certain electrical articles in which a good finish and mechanical strength do not play a predominant part. A liquid resol or a solution of a solid resol in alcohol is masticated with asbestos fibres and the alcohol is for the most part evaporated until a mass remains which is ground into a powder. After being moulded, the object is left by itself in order that the remaining solvent may volatilize. After from 3 to 5 days the material is dry inside and the objects are hardened in an oven for 15 hours at a temperature which is slowly increased up to 190° C (374° F). However, shrinking takes place, which makes the cold moulding process unsuitable for precision work.

b.   The extrusion process.

In Chapter 5 it was pointed out that thermoplastic polymers can be extruded from a machine in endless profiles like rubber tubes. Naturally, the desire has also arisen to put similar methods into practice for thermosetting materials. The difficulty has been to avoid a premature hardening in the press. This problem was solved in Germany; Figure 110 shows an extruder operating according to this principle. The moulding compound passes through a filling hopper and is gradually conveyed by means of a piston which moves back and forth horizontally. The regulation of the temperature in the extrusion channel is very important because first a softening and then a hardening takes place. Moreover, care must be taken that during the extrusion sufficient resistance is encountered to maintain the cohesion in the material. Complicated profiles

(see Fig. 111) of all kinds have been successfully manufactured by the extrusion method; these profiles have found application in the manufacture of car
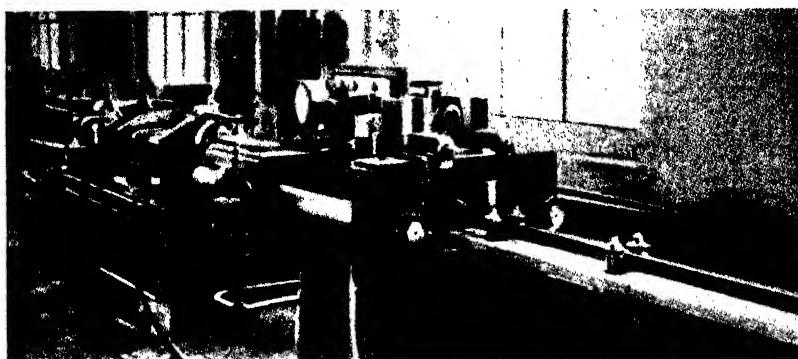
Fig. 110. Extrusion machine for thermosetting materials in action.

bodies and in the electrical industry. Recently pipe connection pieces for application in pipe lines have been designed [1]. In America, a screw type extrusion machine for thermosetting materials has been developed [2] in which very large pieces can be made. A 5 in. tubing with a wall thickness of $\frac{1}{4}$ in. has been extruded at a rate of 2 in. per min.

c. Transfer moulding.

Attempts have also been made to apply the injection moulding method to thermosetting materials. These have succeeded to a certain extent. However, this does not take place in automatic injection machines but in hydraulic presses with special auxiliary constructions. Transfer moulding is coming more and more into use; the advantages are discussed in full on p. 97.

§ 43. PROPERTIES AND USE OF THE FINAL PRODUCTS

The phenol-formaldehyde products belong to the most important group of artificial polymers and this is probably due to the low cost combined with good overall properties. Other groups of polymers sometimes have much superior properties in certain respects, but the phenoplasts distinguish themselves by a happy combination of low cost and good properties.

From a mechanical point of view, they can be used for many purposes, although

Fig. 111. Extruded profiles of phenol-formaldehyde moulding compound.

[1] W. Tochtermann, Kunststoffe, 29 (1939) 71; E. Römer, ibid., 31 (1941) 14.
[2] Plastics Catalog, New York 1945, p. 499.

the high grade representatives are difficult to mould, · owing to the coarse fillers (fabric rags). In electrical respects there exist good average materials, although in comparison with certain thermoplasts these properties

TABLE 40.

BRITISH STANDARD SPECIFICATIONS FOR THERMOSETTING MATERIALS (MINIMUM VALUES)

Indication		Mechanical properties				Thermal properties		Electrical properties		Chemical properties	
		Tensile strength		Impact strength		Temp for 5 mm plastic yield		Break-down at 90 °C	Surface resistivity after imm. in water	Water abs.	Swelling in water
	Unit	kg/cm²	p s i	cm kg/ cm²	ft.lb	°C	°F	Volt/ mil.		mg	inch
G = General type		350	5,000	1.5	0.11	100	212	20	100	200	0.03
GX = Improved general type		490	7,000	1.8	0.13	140	284	60	1,000	120	0.03
M S = Medium shock resistant		420	6,000	4.1	0.3	100	212	20	100	300	0.06
H S = High shock resistant		420	6,000	12.4	0.9	100	212	20	100	350	0.01
H R = Heat resistant		245	3,500	1.0	0.07	180	356	20	100	100	0.002

are inferior, especially in an high frequency field (tg δ, ε). With regard to the heat resistance the phenoplasts are excellent since they are thermosetting.

TABLE 41.

THE MOST IMPORTANT PROPERTIES OF THE PHENOPLASTS

Resin	Filler	Tensile strength kg/cm²	Impact strength Izod notched ft. lb/in.	Continuous resistance to heat °C	Spec. resistance ohm. cm	tg δ at 10^6 Hz (in 10^{-3})
Phenol	none	560	0.55	180	10^{12}	35
,,	wood flour	560	0.32	150	10^{11}	45
,,	slate powder	480	0.6	180	10^{12}	20
,,	asbestos fibres	480	—	180	10^{9}	60
,,	fabric cuttings	560	1—8	120	10^{10}	45
,,	cellulose flakes	560	0.8	150	10^{11}	45
Aniline	none	630	0.3	85	107 at 75°C	7

In Table 40 the *minimum* requirements according to the British standard specifications are mentioned. The materials with higher strength contain coarse fillers like pulp flocks or textile cuttings; an improved heat resistance is obtained by adding inorganic fillers like asbestos fibres. In this table some out-

standing properties have been marked by a frame. A more detailed impression of the influence of the type of filler is given by Table 41 (which is an extract from Table 25).

Although in the beginning the material containing wood-flour was chiefly developed for the electrical industry as a substitute for hard rubber, this material has now also found an extensive use in the household, for fancy articles and moreover as a construction material. A certain limitation of its use is due to the properties of the wood flour, which, being an organic material, is moderately resistant to heating during a long period (limit 150° C). It also imposes in electrical respects certain restrictions on account of its water absorption and in mechanical respects on account of the brittleness of the moulded products. This has led to the development of various complementary materials which in certain respects are better but in other respects have disadvantages, so that every mixture represents a compromise. Viewed as a whole, the wood flour material has remained the most satisfactory and important one.

The resin can also be hardened, without the addition of any filler (see p. 168), but the products obtained are brittle.

The desire for heat resistant materials has been fulfilled by using inorganic fillers instead of wood-flour. Asbestos, mica, and ground slate lead to a good heat resistance up to 180° C (356° F). Ground slate and especially mica furnish better electrical properties than the rather hygroscopic asbestos. The greater specific gravity and brittleness of materials with inorganic fillers are disadvantageous.

Excellent mechanical properties can be obtained by using coarse fillers. Cellulose flakes, paper cuttings, and textiles in various degrees of fineness have brought about great advances in this respect. Fabric cuttings, in particular, have become popular (see Fig. 112); the Izod impact strength can be improved more than 10-fold compared with wood flour mixtures. A disadvantage is that the mouldability becomes worse, the coarser the filler: this has led to the making of pulp preforms. For this purpose, a finely divided phenol-formaldehyde resin is dispersed in the pulp slurry in a beater. The suspension is sucked onto a screen which has the form of the article to be produced. A pulp felt is obtained which can be moulded after drying, leading to products of outstanding mechanical properties. Recently, moulding compounds containing sisal have been developed which give good shock resistant products.

A few words should be said about the use of phenol-formaldehyde moulding materials for *bearings* and *cog-wheels*. For this purpose the types with fabric cuttings are specially suitable, as are the laminated paper and textile

materials (see Fig. 116) about which we shall speak later. The coefficients of friction are, compared to metallic bearings, somewhat higher but, on the other hand, the life time, especially in heavy machines with a slow action, is very satisfactory. The low heat conductivity is a disadvantage but, it is possible to lubricate with water and therefore to cool them at small expense.
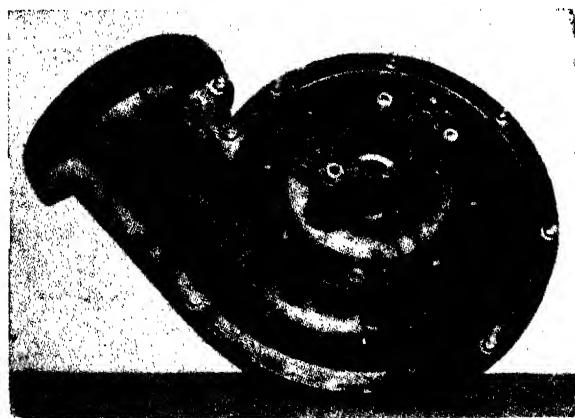
Fig. 112. Centrifugal pump moulded from a phenol resin with fabric cuttings.

The *phenol-furfurole* resins have somewhat different characteristics compared to the P.F.-resins. The B-stage is much less pronounced and the hardening rate is relatively small at the temperature where plasticity is already induced. However, at 180° C (360° F) a very rapid exothermic curing process takes place. This complex of properties makes these resins specially fitted for moulding operations where the circumstances are difficult (transfer moulding). A disadvantage is their black colour.

The *aniline-formaldehyde* resins are thermoplastics with a high softening point and poor flow. At 160° C (320° F), moulding can be achieved at a pressure of 350 kg/cm² (5000 psi), but the mould must be cooled after the shaping of the article.

§ 44. LAMINATED PRODUCTS

Besides profiled products manufactured from moulding compounds, a great need of flat isolated plates has developed. This has led to the so-called laminated paper, fabric, and plywood. These are manufactured in a machine shown in Fig. 113, by impregnating rolls of paper or cloth with a liquid resol or with a solution of solid resol in alcohol and by drying them in an oven. At the same time the resin is hardened somewhat further in order to reach, exactly as on the rollers when making moulding compounds (p. 153), a certain higher condensation degree. However, where laminated materials are concerned the B-state is not generally reached.

The impregnated paper is cut into sheets; several of these sheets are assembled one on top of the other and pressed between flat thin metal sheets in

multiple presses, as shown in Fig. 114. In the beginning the resin softens and flows through the paper so that when the resin content is sufficient the material even develops a glassy appearance. After this the hardening is carried out; then cooling water is added in order to avoid blisters. The laminated materials can also be shaped in shallow moulds.

Fig. 113. Impregnating paper for the production of laminated sheets. (Courtesy Bakelite Ltd)

The laminated products are made in different grades, the properties of which have already been summed up in Table 25 (p. 82). They can easily be punched, and distinguish themselves by great strength; they are used for electrical and mechanical purposes (see Fig. 115 and 116). However, attention should be paid to the fact that the properties differ considerably in two directions. The electrical properties in the direction of the layers are bad, but very good in perpendicular direction. The cleavage, as can be easily understood, is very easy in the direction of the layers. The laminates furnish very valuable construction materials, as they can be machined much more easily than those manufactured from moulding materials.

By pressing a layer of decorated paper on top it is possible to achieve all kinds of artificial effects; such laminated materials are often used for decoration purposes. By pressing between highly polished nickel plates (see Fig. 158, p. 205) a very beautiful high polish can be produced. Thin laminated plates (not thicker than about 2 mm) can be stamped like sheet metal, so that the material is especially suitable for the mass-pro-

Fig. 114. Laminated materials are pressed in flat multiple presses.

duction of flat, isolated parts (Fig. 115). This stamping can be considerably improved by preheating the material.
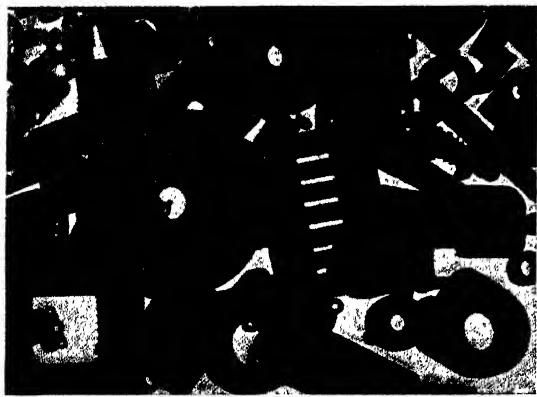
Fig. 115. Insulating components, punched from laminated paper (Bakelite).

For the manufacture of *ply-wood*, at present, thin sheets of paper impregnated with phenol- or urea- formaldehyde resin have become keen competitors of those with the protein (casein, soya bean) glues. This is especially so for outdoor applications, as the latter are not resistant to moisture, heat and mould. Plywood is made under a lower pressure than laminated paper.

A new development along the lines of plywood manufacture is the production of impregnated and *densified plywood* by impregnating the veneer layers through and through; then they are compressed under the high [1] pressure of 100 kg/cm^2 (1,500 psi). A material with a very great impact resistance (Table 42) is obtained ("Compreg").

During the war a new material with outstanding properties was developed in the form of *laminated glass*. Although the starting material is glass, it is remarkable that a shock proof material was obtained, the brittleness of which has become proverbial. First, glass is drawn into very thin, highly orientated fibres of 0.001 mm diameter with a tensile strength of 20,000 kg/cm^2 (300,000

a. Bearing

b. Silent cog-wheels

Fig. 116. Machine parts, made out of laminated phenol-formaldehyde materials.

[1] Sometimes, even a pressure of 200 kg/cm^2 (2800 p s i) is applied.

psi). Experience has shown, however, that this strength spontaneously and rapidly declines at atmospheric conditions to 1/10 of its original value due to chemical action. This causes minute cracks, the notch effect of which is detrimental. In order to avoid this, the fibres are coated with a liquid film of synthetic resin, as they are drawn in the first instance in a hot condition so that no moisture is absorbed. The resin coating serves still another purpose. It supports the fibre continuously when deformation takes place and acts, so to say, as a bridge by which stresses are transferred from one fibre to another. Hence, an even distribution of stresses is obtained throughout the material and no untimely break of certain unfortunately loaded fibres occurs. PRESTON[1] expressed this very characteristically by saying that the new combination is not a glass-reinforced plastic, but rather a plastic supported by glass.

In this way an improvement of the tensile strength of roughly 200% could be obtained in comparison with the laminated materials used hitherto. The CHARPY impact strength could be improved at least in the same ratio as appears from Table 42.

TABLE 42.
SOME PHYSICAL PROPERTIES OF LAMINATES *

	Tensile strength		Compressive strength		CHARPY impact strength
	kg/cm²	lb/inch²	kg/cm²	lb/inch²	lb/inch²
Cotton fabric heavy	800	11,500	2,600	37,000	9
Asbestos fabric	850	12,000	3,400	49,000	12
Fibre glass fabric	2,300	33,000	3,500	50,000	32
Impregnated densified plywood	2,000	30,000	1,600	23.000	40

* C. J. STRAKA, Modern Plastics, 20 (1943) 80.

Particularly in the construction of aeroplanes, the laminates have become competitors of other materials. Here the tensile strength and modulus of elasticity, both divided by the specific gravity, are the decisive physical characteristics. The first measures the strength and the second the stiffness per unit of weight. It appears from Table 43 that impregnated compressed plywood and also resin bonded flax fibres possess mechanical properties comparable with those of steel, aluminium, and spruce, a result which cannot be obtained with cellulose paper and cotton fabric. Glass fabric brings a new improvement in that, apart from the excellent mechanical properties per unit of weight, it also has a high impact strength (Table 42). Moreover it is non-inflammable and possesses a high damping coefficient for noise, a high temperature resistance, and a low moisture absorption. It is thus suitable for tropical conditions.

[1] F. W. PRESTON, Paper read before the Plastics Industry Meeting, Chicago, May 1944.

TABLE 43.

PROPERTIES OF SOME AIRPLANE CONSTRUCTION MATERIALS ON
BASE OF PHENOL

	S.G.	Tens. Strength in kg/cm²/S.G.	Elast. Mod. in 10^3 kg/cm²/SG.	Inflammability
Laminates				
Cellulose paper [1]	1.35	825	90	infl.
Cotton fabric [1] (coarse)	1.38	560	60	infl.
Plywood (impregnated and densified) [2]	1.30	1,900	190	infl.
Flax fibres (Gordon aerolite) [4]	1.43	2,160	290	infl.
Glass fabric [3]	1.75	1,900	290	noninfl.
Materials for comparison				
Aluminum alloy 24 T [4]	2.77	1,560	250	noninfl.
Stainless steel (18-8) [4]	7.85	1,650	270	noninfl.
Aircraft spruce [4]	0.43	1,600	210	infl.

Fig. 117. Laminated tubes in high tension equipment.

[1] L. E. CALDWELL, *Modern Plastics*, **20** (1943) 82.
[2] H. STÄGER in R. HOUWINK, *Chemie und Technologie der Kunststoffe II*, Leipzig 1942, p. 61.
[3] G. B. RHEINFRANK, *Modern Plastics*, **21** (1944).
[4] H. BARRON, *Modern Plastics*, **22** (1945) 243.

For a discussion of bearings and cog-wheels which often are also manufactured from laminated materials, we refer to p. 160.

A new development in the field of laminated materials is *post forming*. Even fully polymerized sheets subjected to temperatures and pressures exceeding normal curing conditions by several hundred per cent retain satisfactory formability [1].

Laminates are also manufactured in the form of rods and tubes. For this purpose the impregnated paper or cloth is wound up under pressure. Subsequently the articles are hardened in an oven. Such tubes have found large scale applications (Fig. 117), combining good electrical properties with great mechanical strength. Hence, they are suitable as construction elements for electrical equipment.

The *laminated aniline resin materials*, as compared with those based on phenol, have the great advantage of being non-tracking, i.e., during the electric flash-over, no conducting path forms on the surface by carbonization. Here we can hardly speak any more of laminated materials because it proved necessary to carry out the impregnation of cellulose in a hollander in such a manner that the resin is embedded between the separate fibres. After compressing, completely homogeneous plates are produced in which laminae can no longer be recognized. Wound up rods or tubes cannot be manufactured from aniline paper because the adhesive capacity is insufficient.

Now that the various laminated materials have been discussed, we must point out a new technique which has opened further wide applications for each of them.

The *low-pressure moulding process* was born during the war out of the need of large, strong, curved articles like airplane fuselages, without using heavy, costly moulds. In the above described "high-pressure laminating" a pressure of roughly 80 kg/cm² (1,200 lb/inch²) is applied. When developing special resins, however, it was found that with a pressure of 10 kg/cm² (140 lb/inch²) or even 1 kg/cm² (14 lb/inch²) a sufficient cohesion between the layers could be achieved.

One of the remarkable features [2] of the low-pressure moulding process is that the tensile strength of the products obtained is only about 25 percent lower when the pressure decreases from 70 kg/cm² (1,000 p s i) to 4 kg/cm² (60 p s i). A further lowering to 0.2 kg/cm² (3 p s i) gives a further reduction in strength of only 10 percent. The modulus of elasticity, however, decreases to $^1/_{10}$ of its original value by decreasing the pressure from 70 to 0.2 kg/cm².

Introducing here the principle of the air bag or fluid pressure moulding, the way was opened for a completely new technique. This air bag moulding,

[1] *Plastics Catalog* New York 1945, p. 938.
[2] J. D. Nelson, *Plastics and Resins Ind.*, 2 (1943) 6; J. D. Nelson and E. F. d'Alelio, *Modern Plastics*, 20 (1942) 45, 122.
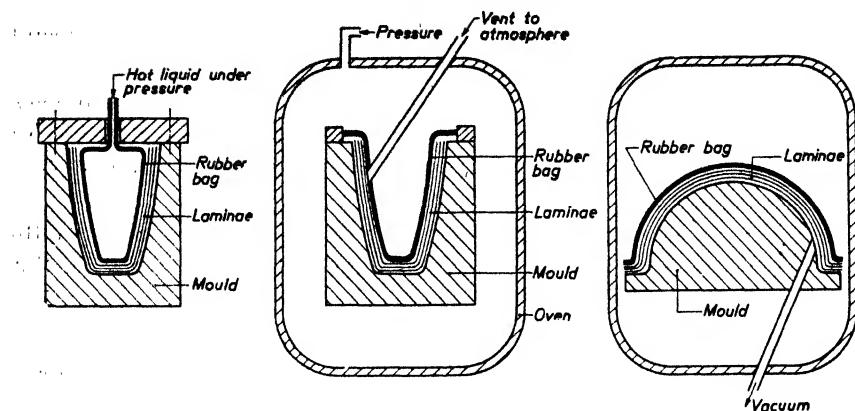
a. Internal hot air or   b. Hot air pressure (in the oven)   c. Vacuum pressure
   liquid pressure   (in the oven)

Fig. 118. Some principles used in low-pressure moulding.

as pictured in Fig. 118, makes use of a cheap mould of wood, plaster, or metal. The resin-impregnated laminae are placed *in* (Fig. 118a) or *on* (Fig. 118c)

the mould. This is covered by a rubber bag and vacuum or pressure (air or fluid), depending on the technique, is applied in such a way that the rubber bag is pressed against the laminae. After curing, the object is removed from the oven. Fig. 119 shows a boat moulded in this way.

It can be predicted that a great development of all kinds of laminated products will take place along these lines. The method is not restricted to phenolic materials but it can also be applied to the ureas, melamines, unsaturated polyesters, and allyl resins. Experiments are now being made to bring about the curing by the addition of a catalyst which would avoid the use of ovens (see page 173).

Fig. 119. Low-pressure moulded boat.

High frequency heating (see p. 98) has opened completely new fields [1] for all these kinds of materials, since formerly the manufacture of thick articles was especially difficult. In laminated materials the heat had to be introduced by convection, an extremely slow process. Applying high frequency heating, however, the heat development takes place instantaneously throughout the material and this advantage compensates for the fact that the efficiency of the high frequency system is only about half that of electrical resistance heating. The final result is shown [2] in Fig. 120, from which it appears that the curing time can be reduced to one fifth by preheating the material at 150° C instead of at 110° C. A plywood plant in the U.S.A., with a 600 KVA high frequency installation is turning out stacks of phenol-resin-bonded panels, 12 inches thick, at the rate of 15 bundles per hour.
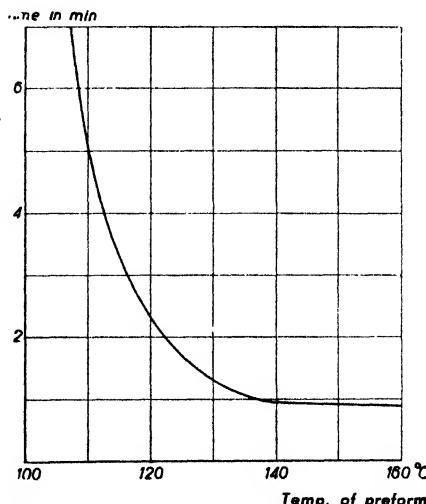
Fig. 120. Relationship between minimum curing time of a 2.54 cm (1 inch) block and temperature of the preform.

§ 45. CAST AND MOULDED RESINS

Usually, moulding compounds containing fillers are used, but pure hardened resins without additions have also found application for making profiled objects.

The oldest process is the manufacturing of *cast resins* by pouring a liquid resol into moulds of glass, lead, or nickel, and hardening it in the mould. The hardening must be effected very slowly so that no gas bubbles form, as these would spoil the material. The reaction can be conducted in such a manner that clear, transparent products are obtained which can be coloured at will. However, it is also possible to effect a separation of water, which leads to an ivory-like product. When very deep tubular moulds are used, long profiled rods are manufactured from which all kinds of objects can be machined (Fig. 121). Another way is to use moulds of plaster of Paris which can eventually be lined with a coating of rubber (applied as latex). At present, very large objects of complicated shapes are produced. Hollow articles can

[1] See for a complete description, *Plastics Catalog*, New York 1945, pg. 479.
[2] H. BARRON, *Modern Plastics*, New York 1947, p. 591.

be made by using moulds with a detachable inner core. The liquid resin is poured between core and mould; after hardening, the core is first removed and then the casting is drawn from the mould. The use of cast phenolics has not remained limited to luxury objects like buttons and imitation jewelry but there are also industrial applications based on the chemical resistance and the electrical insulating properties. At present, mechanical punches are made from cast phenolics.

The desirable properties, especially the magnificent colours and the silky gloss, have led to attempts at *moulding the unfilled resins*. This has proved rather difficult; it seems that the last traces of water formed in the condensation process are absorbed by the fillers, and this opportunity does not exist in pure resins. So it is not easy to produce a readily mouldable material that gives cured products without blisters. However it has proved possible to overcome these difficulties, for the greater part, by masticating the resins a very long time on the rollers (Fig. 106, page 153) and adjusting the rollers very closely so that water vapour can escape easily. In spite of these precautions, the moulding operation still offers difficulties.

It is notable that in the cast as well as in the moulded resins the impact resistance does not give a correct idea of the behaviour of materials in practice. Only by determining the notch effect is the brittleness, which appears in practice, expressed numerically.

Fig. 121. Products machined from cast phenol resin.

Moulded resin articles have, here and there, found technical application in cases where glass proved to be too brittle, where a water clear transparency and low prices are not necessary or where special requirements are to be met (low absorption of moisture). However, the main application is for trinkets.

The unfilled aniline resins possess some important advantages with respect to electrical properties, thus creating new possibilities for application. They are non-tracking and show low dielectric losses. Moreover, they are shock- and alkaliproof, but can be moulded less easily, requiring a very high pressure. They are to be considered as thermoplastics with a high heat distortion point ($100°$ C $= 212$ °F) and a high impact strength (0.33 ft. lb per inch of notch Izod). For the properties, see page 158.

§ 46. L A C Q U E R S

The phenol-formaldehyde resins as such can be used as lacquers[1]. To this end, either liquid resols (see p. 149) or solid resols, dissolved in alcohol, are applied. In special cases the hardening is effected with the aid of acids.

Such lacquers are very hard and nail-proof but they are also brittle. Of course, an attempt to remedy this by using plasticizers[2] succeeded only to a certain extent, as the softeners are insoluble in the hardened resin and thus eliminate themselves during the hardening process. Later research has shown that the desired softening in the C state is only possible when the plasticizing molecules are *built into* the resin macromolecule (internal softening, see p. 59); we shall come back to this again.

The resols also have the disadvantage of being compatible only with substances of a certain polarity like alcohol, and not with fatty oils. If we take into consideration that for a long time the desire has existed to combine synthetic resins with many other primary products in the paint industry, like oils, natural resins, etc., it becomes clear that here an extensive field of research has opened. The development has led to three principal types, which are all soluble in, and reactive with, oils.

a. The alkylphenol resins

b. The plasticized phenol resins (with "built-in" softeners)

c. The modified phenol resins (combined with natural resins).

a.   Alkylphenol resins.

In order to obtain compatibility with hydrocarbons and fatty oils, it is necessary to introduce alkyl groups into the phenol nucleus in order to make it less polar. One can proceed according to the scheme of Fig. 122, showing the formation of resin from p-tert.-butylphenol and formaldehyde.

The solubility in oil may be attributed to the fact that by means of the alkyl groups the attracting dispersion forces between the phenol nuclei are screened off so that the oil can enter between them. Instead of alkyl groups, aryl, arylalkyl and alicyclic residues can also be introduced. The alkylphenol resins are preferably used for the manufacturing of tung oil lacquers; the resin is dissolved in preheated oil and then the mixture is heated at a temperature

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[1] A tabulated summary regarding the manufacturing conditions, the resin properties and the acquired varnish properties is given by V. H. TURKINGTON and J. ALLEN, *Ind. Eng. Chem.,* **33** (1941) 966.

[2] The expression *plasticizing* is familiar in the lacquer industry. In our opinion it would be better to speak here of *elasticizing* because the films become more highly elastic by the addition of the substances involved. A neutral term is *softening* which refers to both effects.

of 250° C (482° F), as a result of which water is liberated, leading to a strong foaming. During this boiling process a chemical reaction between resin and
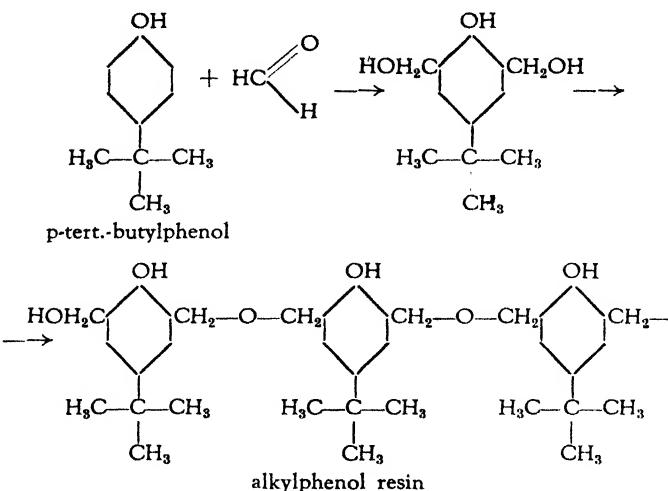
Fig. 122. Formation of an alkylphenol resin from p-tert.-butylphenol.

oil takes place which may be explained [1] by the interlinking of the eleostearic acid chains present in wood oil by means of the chroman ring, according to Fig. 123.
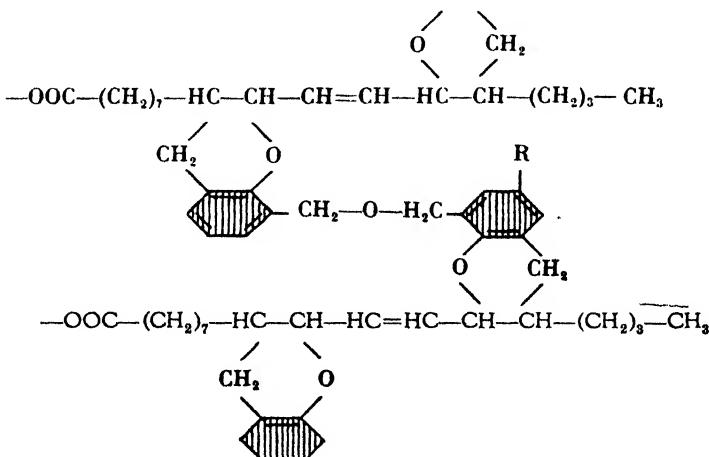
Fig. 123. Interlinking between eleostearic acid and alkylphenol resin by means of the chroman ring formation (benzene nuclei of the alkylphenol resin are indicated by hatching).

[1] A. GRETH, Kunststoffe, 28 (1938) 129; ibid., 31 (1941) 345.

To explain this chroman ring formation, it may be mentioned that, generally speaking, a condensation according to Fig. 124 is assumed between o-hydroxy-benzyl alcohol (or its derivatives) and doublebonds. Consequently, as regards the phenol lacquers, possibilities for many reactions exist, as all drying oils and also the greater part of the natural resins contain double bonds.
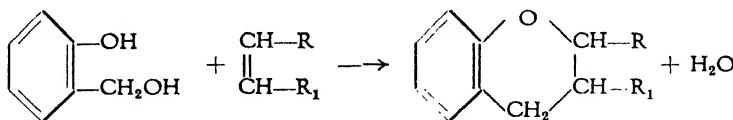
Fig. 124. Chroman ring formation.

With regard to Fig. 123, it should specially be pointed out that the benzene rings are mutually interlinked by long bridges in consequence of which the macromolecule obtains a certain mobility and the brittleness disappears. The chain-like residues are internal softeners (see p. 59).

b. Plasticized phenol-resins.

A material like that in Fig. 123 might be conceived as a plasticized [1] phenol-resin, but in the majority of combinations the oily part preponderates to such an extent that we can hardly speak any more of a resin.

The circumstances are different with regard to the types now to be dis-cussed. By etherification, certain monoalcohols can combine with alcohol-soluble resol alcohols, e.g., according to Fig. 125. Into these, plasticizing materials are introduced whereby the predominantly resin-like character can be mostly maintained. Certain chain-molecules, like unsaturated fatty acids, polyvinyl or polyacrylic compounds, alkyd resins, and similar ones are used as plasticizers. In this connection a very favorable circumstance is the fact that the etherified phenol-resin can dissolve the fatty acids. When alkyd-resins are introduced it is presumed that an etherification takes place between the hydroxymethyl phenols and the hydroxyl groups of the alkyd-

di(hydroxymethyl)-phenol   propyl alcohol
Fig. 125. Alkoxylating of the resol alcohol.
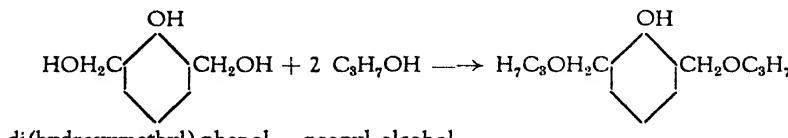
resins. Once the chains are introduced, they conserve the elastifying properties during the subsequent hardening (internal plasticizing, see p. 60). As the phenol content is decisive for the hardness and chemical resistance, it should

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[1] In our opinion it is better to speak of an elasticized resin here also because the material becomes more highly elastic.

be kept as high as possible; in practice, good results are obtained with 25%
softener content.

When comparing the plasticized phenol resins with the alkylphenol resins,
it appears that the difference is not really fundamental; in both instances
we finally obtain modified phenol bodies, with built-in chain molecules. Only
the character and the degree of the modification are different.

c. Phenol resins, modified with natural resins.

By the so-called modified phenol resins we understand combinations of
phenol-resols with natural resins, in particular colophony. This contains
abietic acid (for formula see p. 19) which, being unsaturated, can build up
chroman rings with phenol-alcohols, as shown in Fig. 126. The CH_2OH-group
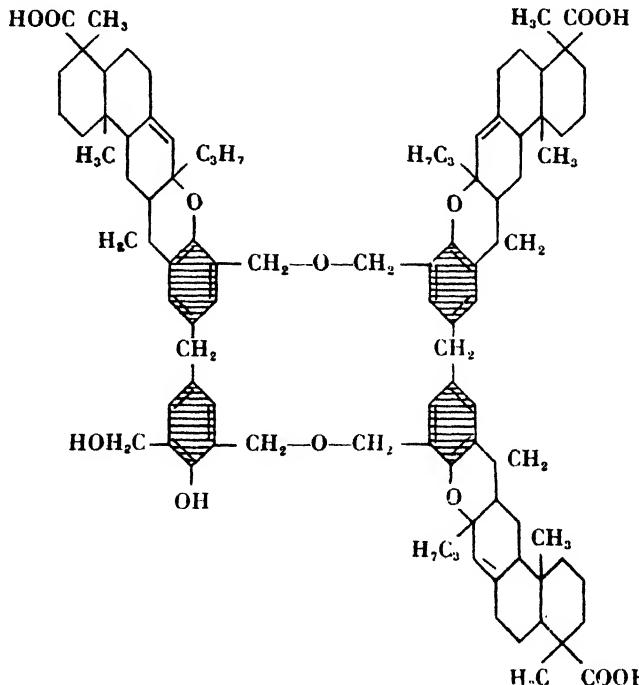
Fig. 126. Building-up of a modified phenol-resin on the basis of abietic acid and phenol resol
(the benzene nuclei of the phenol resols are hatched).

can react still further and links itself to another similar complex. Moreover
the carboxyl groups are also capable of reaction, so that a three-dimensional
molecular growth is possible; the content of the colophony can amount to
80%. A reaction with fatty acids or polyalcohols can also occur, by means
of which the bodies become suitable as lacquers.

From the above mentioned raw materials, the lacquers are manufactured

either by dissolving in alcohol, in petrol, or, where necessary, with the addition of pigments or by boiling with suitable oils.

The importance of these synthetic resins for the lacquer industry may be demonstrated by the following figures: in 1932 only 13 million kg of copal were used in the U.S.A. as against 48 million kg of modified resin esters.

§ 47. OTHER APPLICATIONS

Besides those mentioned already, the synthetic resins based on phenol find various other special applications of which the following may be mentioned:

1. An important application is in the form of a paste. For acid-proof linings one starts from liquid resins, to which are added asbestos or other acid-proof filling materials. The paste can be kneaded and moulded by hand.
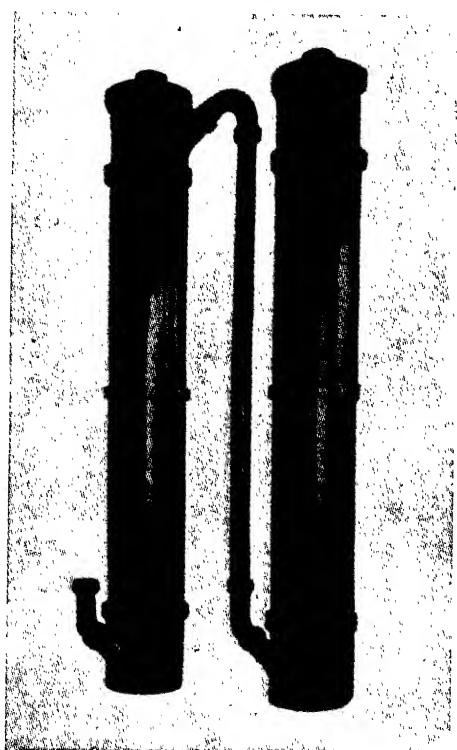
Fig. 127. Objects made of "HAVEG".

The hardening is carried out either by means of heating or by adding acids (e.g., p-toluenesulphonyl chloride [1]). The layer which forms, is somewhat porous and therefore the wall is made rather thick, e.g., 2 mm, in order to obtain a sufficient impermeability. Fig. 127 shows some objects manufac-

[1] For recipes see: G. M. KLINE, Brit. Plastics, 18 (1946) 171

tured by this method. At present, the process is not only limited to lining purposes. Just as with clay, all kinds of articles can be formed with the aid of simple wooden or metal moulds and so very large constructions can be made at a reasonable cost. The articles, manufactured according to this "HAVEG" process (Fig. 127) are proof against the majority of acids except concentrated nitric, sulphuric, and chromic acids. In the construction of chemical apparatus very good results have thus been achieved.

2. *Grinding wheels*. Diamond powder can be mixed with a liquid resol until a paste has formed. It can then be moulded to form grinding wheels for hard metal tools. For this purpose, 50% of rather coarse diamond powder, 25% of ground quartz and 25% of phenol resin binding agent are mixed together. For economic reasons the thickness of the layer of diamond powder which must be put on the grinding wheel, should not exceed 2 mm. In this manner, grinding wheels are obtained which can easily make 6,000 revolutions per minute.

3. In a similar manner *magnets* can be manufactured by mixing the magnetic metal dust with 15 to 25 per cent by volume of phenol resin and moulding under high pressure. Naturally not all properties of a metallic magnet can be achieved, as a certain percentage of the volume consists of non-magnetic material. On the other hand, however, advantages exist; the body really consists of a collection of small separated single magnets. To these advantages can be added the ability to be moulded and the possibility of pressing in soft-iron pole-shoes and other parts. Recapitulating, it can be said that such pressed magnets possess the equivalence of Orstit magnets, provided their length is taken as 10%, and their cross-section about 50% greater.

4. The phenolic resins have found application as *ion-exchangers*[1], being competitors of the zeolites. The phenol-formaldehyde resins can replace cations by hydrogen ions by means of their OH-groups, whereby the salts are converted into the corresponding acids. On the other hand, acids or anions can be removed by chemical combination with, e.g., the NH_2-groups of m-phenylenediamine condensed into an insoluble resin with formaldehyde.

In this way, water can be purified and it is also possible to absorb polar organic constituents from solutions, decolorizing them or making them tasteless. In this respect they show a certain selectivity which has led to special applications. Since such exchangers can be regenerated by dilute acids or alkalis, they have found ready application in industry.

5. *Foams* of the rigid type are made from phenolics and from ureas by expanding processes.

[1] F. J. MYERS, *Ind. Eng. Chem.*, Ind. Ed., 35 (1943) 858.

CHAPTER IX

POLYMERS BASED ON CARBAMIDES, ETC. [1]

§ 48. RAW MATERIALS

The plastics to be discussed in this chapter are based on the reaction of urea, thiourea or melamine (aminotriazin) with formaldehyde. Urea nowadays is usually obtained from ammonia and carbon dioxide in the presence of water, as in the scheme of Fig. 128.

$$CO_2 + 2NH_3 \underset{\leftarrow}{\rightarrow} H_2N—COONH_4$$
$$H_2N—COONH_4 \underset{\leftarrow}{\rightarrow} H_2N—CO—NH_2 + H_2O$$

Fig. 128. Modern urea synthesis.
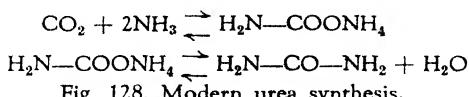
The second reaction takes place in a temperature range of from 135 to 150° C (275—302° F) under pressure and leads to an equilibrium mixture containing about 50 per cent of urea. The unconverted carbon dioxide and ammonia are brought back into the process. The urea is obtained in solution and purified by crystallization. This process necessitates the use of corrosion-proof material; this originally caused great difficulties which have now been overcome. The quantity of urea required for the manufacturing of plastics is only a small part of the total production which is chiefly used for fertilizers.

Thiourea is made from calcium cyanamide and sulphides in the presence of weak acids according to Fig. 129.

$$CaN—CN + Na_2S + 2CO_2 + 2H_2O \rightarrow H_2N—CS—NH_2 + CaCO_3 + Na_2CO_3$$
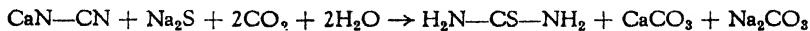
Fig. 129. Thiourea synthesis.

For plastics the thiourea is not very important, since it is added only in small quantities because of its higher cost.

2,4,6-triamino-2,3,5-triazine (melamine) is obtained from dicyanodiamide in accordance with the equation in Fig. 130.

This compound has three amino groups capable of reaction and therefore is well suited for the formation of resins.

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[1] See *Plastics Monograph* No. 2. Inst. Plast. Ind., London 1947.

$$3 \ NH = C \diagup_{NH}^{NH_2} \diagdown CN \qquad \longrightarrow \qquad 2 \ NH_2 - C \diagup_{N}^{C - NH_2} \diagdown_{N}^{N} \diagdown_{C - NH_2}$$

dicyanodiamide   melamine
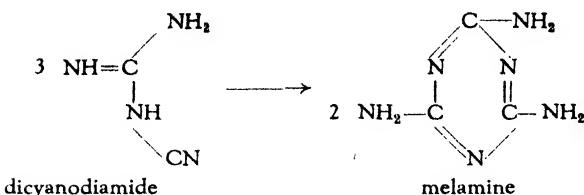
Fig. 130. Synthesis of melamine.

§ 49. THE MANUFACTURE OF RESINS AND MOULDING MIXTURES

a. Resins.

The condensation process is much more difficult to control than that for the phenol-formaldehyde resins because the development of the reaction is strongly influenced by the pH of the solution. Moreover, a modification in the reaction temperature can here lead to entirely different products. There-fore, it is a difficult task to conduct the reaction in such a manner that resins are formed with the correct degree of condensation and the right proportion of OH groups necessary for effecting the hardening.

It is now supposed that, according to circumstances, either mono-hydroxymethyl urea I or di-hydroxymethyl urea II is formed first. However, there is also a tendency for methylene urea (III or IV) to be formed.

I. $CO \diagup_{NH-CH_2OH}^{NH_2}$ II. $CO \diagup_{NH-CH_2OH}^{NH-CH_2OH}$

monohydroxymethyl   di-hydroxymethyl

III. $\left[CO \diagup_{N=CH_2}^{NH_2} \right]_x$ IV. $\left[CO \diagup_{N=CH_2}^{N=CH_2} \right]_x$
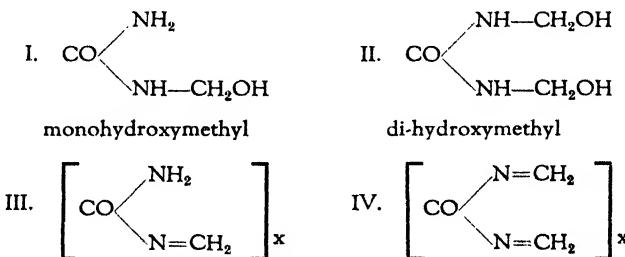
Fig. 131. Possible stages in the resinification of urea.

The chief point is to adjust the reaction conditions in such a way that intermediate compounds (the hydroxymethyl-methylene ureas, Fig. 132) are formed, containing one or more hydroxymethyl groups and imino groups capable of reaction. They can condense with the elimination of water and formaldehyde; the macromolecule which then forms is represented in Fig. 133.

This macromolecule has a structure which in a colloidal respect can be

V. $\begin{array}{c} NH-CH_2-NH \\ | \qquad\qquad | \\ CO \qquad\quad CO \\ | \qquad\qquad | \\ NH-CH_2-N-CH_2OH \end{array}$ VI. $\begin{array}{c} NH-CH_2-N-CH_2OH \\ | \qquad\qquad | \\ CO \qquad\quad CO \\ | \qquad\qquad | \\ NH-CH_2-N-CH_2OH \end{array}$
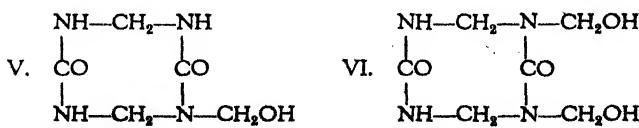
Fig. 132. Hydroxymethyl methylene compounds.

compared with that of the phenol-formaldehyde resins, and also contains "Lockerstellen", leading to a much lower strength than would be expected theo-
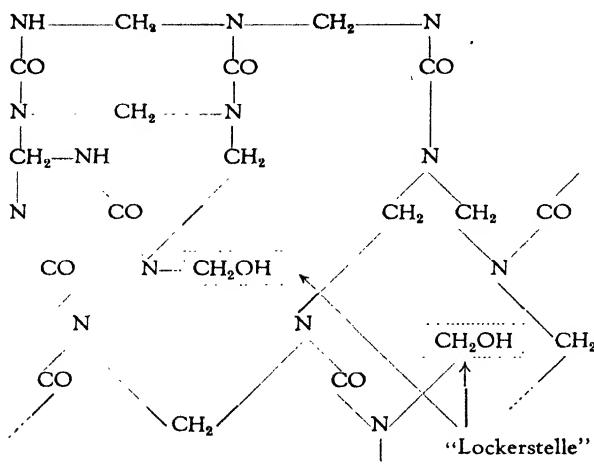
Fig. 133. The urea-formaldehyde macromolecule (with a "Lockerstelle").

retically. As will appear during the discussion of the heat resistance, however, fundamental differences also exist. This is probably due to the somewhat unstable bonds at the nitrogen atom. On p. 181 we shall see that an exact degree of hardening in the press is necessary for the water-resistance of the finished products. This can perhaps be explained by the necessity, as regards these resins, to free the macromolecule from hydroxymethyl groups.

The formation of resins from thiourea develops in a similar manner and does not need any special remarks. With regard to the condensation of amino-triazine, it is also supposed that, primarily, hydroxymethyl groups are formed, thus forming hexa-hydroxymethyl melamine; here also the original watersolubility decreases during the further condensation. The macromolecules represented in Fig. 134 are less sensitive to water and temperature than the urea-formaldehyde products; this is probably due to more extensive interlinking. In our opinion this calls for further
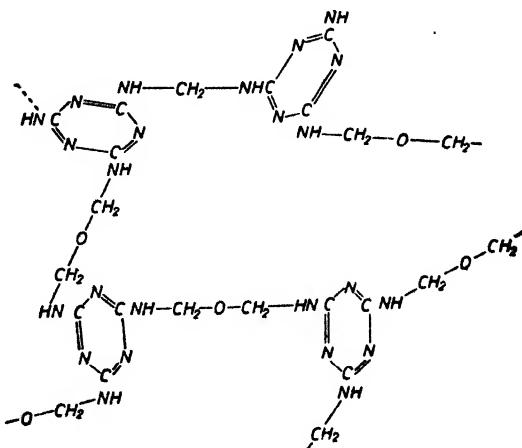
Fig. 134. Structure of the melamine resin macromolecule.

study, however, as there exists already in the urea-formaldehyde resins the possibility of interlinking.

b. Moulding materials.

The manufacture of moulding compounds is very simple, since the resins are obtained in an aqueous solution and the fillers can be impregnated immediately. In principle, wood flour may be used as filling material, but its application has remained rather limited because the main value of this group of plastics lies in the ability to manufacture bright and soft nonfading colours. These advantages are only produced when pure cellulose is used as filler, in which case a beautiful result is achieved, the compound being somewhat transparent. For trinkets, fancy boxes, etc, this is specially important. A typical compound is the following:

TABLE 44.

U. F. MOULDING POWDER

Urea	120	g
Formaldehyde (30%)	300	,,
Cellulose (80—85% α)	105	,,
Ammonia (S.G. = 0.9)	5.4	,,
Zn stearate	0.5	,,
Hexamethylenetetramine	1.5	,,
ZnO	0.1	,,

After having impregnated the cellulose with the resin solution, which can be done in a kneader, the compound is dried in ovens and at the same time condensed further until the exact desired degree of polymerization is reached. This — as stated already — is particularly important. In contrast to the phenol-formaldehyde resins, no metal mixing rollers can be used here because the delicate shades would be destroyed. A vacuum drying oven is used and here the problem is to heat the crumbs of material slowly and equally so that the outsides of the particles are not hardened before the water has had the opportunity to diffuse from the core. Particles condensed insufficiently lead to a bad surface on the moulded articles and little resistance against moisture; particles condensed excessively strongly reduce the flowing power.

After the drying process the crumbs are ground; this also requires care in order to avoid any dirt. For this reason ball mills lined with porcelain (see Fig. 135) are used instead of high speed disintegrators. The mills must be closed because otherwise moisture is attracted which would lead to a clogging together of the material.

During this grinding process, different ingredients, such as lubricants, accelerators and dyes, can be added. The flow sheet is represented in Fig. 136.

As mentioned already, mixtures of urea and thio-urea resins are often manufactured in order to obtain compounds with better properties.

Great difficulties in the manufacture of moulding compounds are caused

Fig. 135. Ball mills for making urea moulding compounds.

by the requirements necessary to ensure a satisfactory appearance of the finished products. In order that every new charge obtains exactly the same colour, it is necessary to control carefully the conditions of manufacture and to avoid dirt.
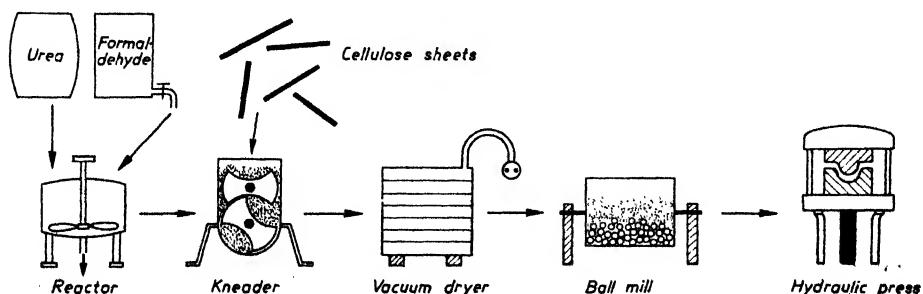
Fig. 136. Flow sheet of carbamide moulding compounds.

In consequence of all these factors the compounds are more expensive than those based on phenol-formaldehyde and are used only for special pur-

poses in which the appearance plays a predominant part. It is possible to work on the mixing rolls with wood flour, thus making cheaper, dark-coloured mixtures, but these have not become popular because of their unattractiveness. Since, furthermore, the properties of the finished products show certain technical disadvantages (low heat resistance), the urea compounds still play a secondary part. The development of melamine resins has removed these objections for the greater part, and the present price situation opens the way for a more general application (see below).

§ 50. MOULDING

The carbamide-plastics, also called *aminoplasts*, are most suitable for compression moulding, but not for injection moulding; they are used only occasionally for the extrusion process.

In general, the tabletting and moulding takes place as shown on p. 68 for phenol-formaldehyde resins. The moulding, however, is much more difficult because once the temperature has been fixed the moulding period must lie within very narrow limits. If it is too short, then the condensation is carried through insufficiently and the finished object is very sentitive to moisture; this is probably due to the presence of free OH groups, as mentioned on p. 177. If, however, the moulding time is too long, then the resin is decomposed, perhaps because the nitrogen bonds are not very stable. The higher the temperature the narrower are the time limits, as is shown in Fig. 137.
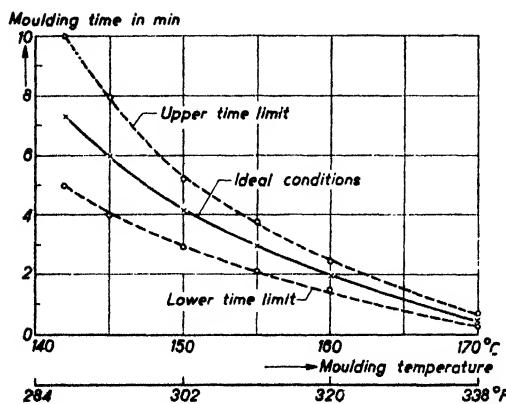
Fig. 137. Dependence of the moulding time on the temperature during the moulding process of urea compounds [1].

These difficulties have considerably limited the applications of the urea compounds; thick-walled pieces cannot be manufactured, as the exterior layer is decomposed in the press, while the interior is not sufficiently hardened. Thick pieces therefore always show tensions and the core easily attracts water, leading to the cracking of the article. Another difficulty is that the moulds corrode, so that rust-proof steels are needed. This is especially the case with compounds containing thio-urea. However, if care is taken to heat the

[1] Unpublished experiments.

moulds evenly throughout and if all requirements regarding temperature and control of time are observed, then thin-walled pieces can be manufactured faultlessly. Fig. 138 shows a hydraulic press in operation. Fortunately, we

Fig. 138. Moulding of aminoplasts.

have at our disposal a very simple test for determining the exact degree of curing, namely, by means of the boiling test. Fig. 139 shows a goblet which has been moulded in a unevenly heated mould after having been boiled in water for 30 minutes. The bottom- and top-zones are hardened insufficiently and therefore cannot resist the boiling test (in contrast to the middle-zone).

During the manufacturing process it is therefore necessary to control regularly the current production by means of boiling tests.

These difficulties have stimulated the development of the melamine moulding compounds; for these, there is a greater range of temperature within which it is possible to mould them satisfactorily. Moreover, the melamine masses harden more quickly.
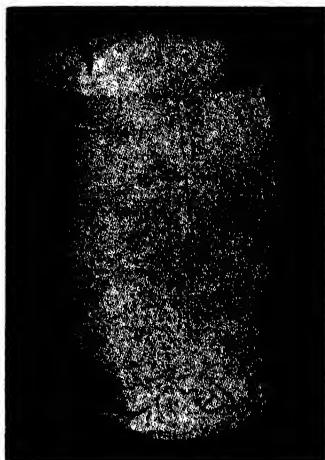
Fig. 139. The bottom- and top-zones of this goblet have been hardened insufficiently because of unevenly heated tools, as detected by the boiling test.

§ 51. APPLICATION AND PROPERTIES OF THE FINISHED PRODUCTS

In the course of this chapter the fields for the principal applications have already been mentioned; specialities are fancy articles, pastel coloured table crockery, furniture parts, and odorless packings (see Fig. 140), etc. The most important properties have been presented in Table 45; the slight heat resistance of these resins is immediately obvious.

In electrical and mechanical respects, the properties are comparable with those of phenolics filled with wood flour (see Table 45).
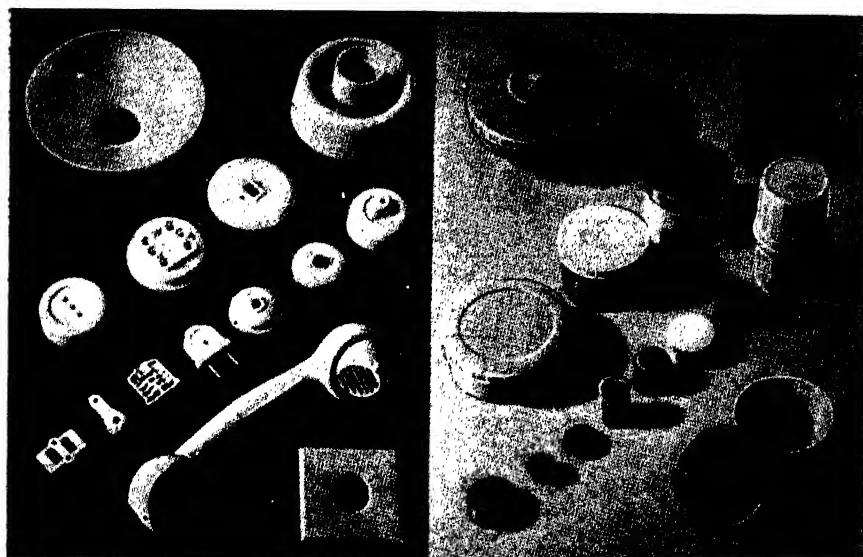
Fig. 140. Articles manufactured from aminoplasts.

TABLE 45.

THE MORE IMPORTANT PROPERTIES OF THE AMINOPLASTS

Material	Tensile strength kg/cm^2	Imp. strength Izod notched ft lb/in	Continuous resistance to heat., °-C	Spec. resistance ohm. cm	tg δ at 10^6 Hz x 10^3
Urea-formaldehyde resin with cellulose	600	0.3	82	10^{12}	40
Melamine resin with cellulose	500	0.4	100	10^{12}	40
Phenol-formald. resin with wood flour (for comparison)	560	0.32	150	10^{11}	45

The annual turnover can at present be estimated at about 10% of the consumption of phenol-formaldehyde resins. As said already, the melamine

plastics distinguish themselves from the ureas by a greater heat resistance and also by a greater hardness, the latter often being an advantage, but sometimes a disadvantage. The resistance to hot water is also greater and a special feature is their arc resistance. Consequently, the melamines are applied where the ureas fail. In this respect it is interesting to make a comparison of the prices. From p. 246 it can be seen that in the U.S.A. the melamines sell only at a 10% higher price than the ureas. In Europe the price difference is about 40%.

§ 52. OTHER APPLICATIONS
a. Laminated products.

Exactly as is the case with phenol-formaldehyde resins, laminated sheets can be manufactured from the carbamides by impregnating paper or tissue with the resin initially in the liquid state. For urea laminates in the pressing operation, the same care has to be taken with regard to temperature- and time-limits, as mentioned on p. 180. By pressing a coloured or printed layer on top, decorative effects can be achieved. The well-known table-tops in restaurants, where these laminates are glued on plywood, are examples. Here especially have the melamines brought about a great improvement due to their resistance to hot water. A growing application is the engraving of name shields from laminates in which a top layer has been pressed on inner layers of a different colour. The characters are engraved deeply so that the inner layers become visible, leading to beautiful contrasts.

Fig. 141. Melamine bonded construction.

Another application of laminated products is for plywood glue . (Kaurit) a product in which the further condensation is effected by heating or in the cold by adding ammonium chloride[1]. Fig. 141 presents the erection of melamine

[1] For recipes see G. M. KLINE, *Brit. Plastics*, 18 (1946) 174.

resin bonded construction elements. Especially for melamine adhesives, the prospects are excellent, as this material meets the requirements for the Army and Navy specifications.[1] It is scarcely necessary to say that the development of low pressure moulding opens the way for further development of the melamines.

b.   Lacquers.

Originally, it was hardly possible to introduce the carbamide resins as lacquers because the aqueous solutions were incompatible with the usual polymers and plasticizers and because under the influence of moisture the carbamide resin films showed a tendency to crack. The compatibility has been improved by effecting the formation of the resin in certain organic solvents like butanol, a process during which an introduction of the butanol molecules into the urea resin molecule seems to occur; in this case we speak of modified carbamide resins. As these are at the same time miscible with certain plasticizers, an extensive choice of lacquer raw materials has resulted. Particularly as an addition to nitrocellulose have they been succesfully introduced on account of their lustre, their hardness, and lack of colour. Moreover, a great number of co-condensation products with other synthetic resins are known; those with phthalic acid and with phenol-resins may be mentioned here.

The melamines have also found application in lacquers, especially as an addition to alkyd resins, by means of which light coloured, non-fading, and heat-proof enamels (up to 200 °C; 392 °F) for muffling purposes, can be obtained. With a small proportion of alkyd these lacquers are hard; with predominant proportions they are flexible and can be used for textiles, artificial leather, etc. A new use is for the treatment of paper, which then retains a high strength when wet. For this purpose a colloidal dispersion is used, the quantity of the resin being 1 to 2 per cent of the dry weight of the paper. The increased strength permits the use of lighter weight paper, leading to savings in pulp.

c.   Textile improvers.

The use for *improving the creasability of textiles* is one of the most important applications of ureas and melamines. Cotton or rayon fibres are impregnated in a swollen condition with carbamine condensation products soluble in water and are then hardened. After drying the textile, its creasability is diminished considerably (Table 46). The improvement in resistance against wear is estimated to be four- to five-fold. This action may perhaps be explained by assuming an interlinking between the resin and the fibres. In this respect,

[1] A N · N · P 511a; U.S. Stand. C S 45—38.

the vulcanization of rubber may be considered, where the elastic behaviour is also improved by vulcanization.

This treatment also considerably reduces the shrinkage of the textiles when washed, especially of wool.

Starting from a methylated hydroxymethyl melamine:

$$
\begin{array}{c}
CNH_2 \\
\diagup \quad \diagdown\diagdown \\
N \quad\quad N \\
\parallel \quad\quad | \\
H_3C\ O\ H_2C\ HN\text{-}C \quad\quad CNH_2 \\
\diagdown \quad \diagup\diagup \\
N
\end{array}
$$
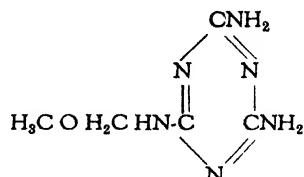
which is converted into the insoluble polymer by means of a catalyst, the following improvement was obtained[1].

TABLE 46.

DECREASE OF WOOL SHRINKAGE BY TREATMENT WITH MELAMINE DERIVATIVES

% Methylated hydroxymethyl melamine	% Shrinkage after 30 min washing
Untreated	18
5 %	3.5
10 %	2.1

The theoretical explanation of this action is not yet known. Other important applications in the textile field lie in the possibility of using amino-resins as stiffening agents or for the matting of artificial silk. It is supposed that during the latter process the minutely distributed resin particles are smeared on the textile fibres, in consequence of which the light is diffused and the fibres have a matted appearance.

d. Wet-strength paper.

Melamine-formaldehyde resins have found an important application in improving the strength of paper in the wet condition. Between 0.5 and 3 per cent of resin is added to the pulp and polymerisation is effected during the drying process on the paper machine. A further condensation can take place in the storehouse at room temperature. The strength in dry condition is improved by approximately 15 per cent. In the wet condition the strength

[1] E. P. JOHNSTONE, *Am. Dyestuff Repr.*, 33 (1944) 301.

is 3 to 15 times greater than that for the untreated paper[1], see Table 47. A disadvantage of the process is that waste paper cannot be re-used as raw material in the ordinary way. Substituting the melamine resin by urea resin makes this possible because urea resin can be dissolved with alkali. The beneficial effect of urea resin on the wet strength is, however, small.

TABLE 47.

IMPROVING THE WET-STRENGTH OF PAPER BY MEANS OF MELAMINE RESIN

Paper	Relative tensile strength (original dry=100)			
	Untreated		With 3% resin	
	Dry	wet	Dry	wet
From rags	100	4	130	60
From sulphate cellulose	100	3	122	37
Kraft	100	8	116	25

e. Expanded resins.

Urea and melamine resins can be used to make foams of the rigid type. These foams are considerably weaker than those made of ebonite, polyvinyl chloride, or cellulose derivatives.

[1] G. E. FROMM, Pulp & Paper Mag. Canada (1945).

POLYMERS BASED ON CARBOXYLIC ACIDS

§ 53. FROM NATURAL OILS[1]

The drying oils (linseed, perilla, tung, oiticica oil) contain triglycerides of unsaturated fatty acids. In linseed oil, for example, the glycerine can be attached to the following three fatty acids chains:

	acid residue	inactive part	active part	chain end
Oleic acid	ROOC—$(CH_2)_7$—	$(CH=CH—CH_2)$—		$(CH_2)_6$—CH_3
Linolic acid	ROOC—$(CH_2)_7$—	$(CH=CH—CH_2)_2$—		$(CH_2)_3$—CH_3
Linolenic acid . . .	ROOC—$(CH_2)_7$—	$(CH=CH—CH_2)_3$—		CH_3

Fig. 142. Fatty acid chains in linseed oil.

The part of the molecule indicated as being active is of special significance. In the two latter acids, several active parts exist and therefore the number of possibilities for interlinking is very large here. In Fig. 123, p. 170 it could be shown how, for the manufacturing of lacquers, phenol resins were built into fatty acids as bridges. The number of reactive spots is greater in conjugated systems because, as was pointed out especially by KAPPELMEIER[2], with double bonds these systems show a tendency to undergo the DIELS-ALDER-reaction, in accordance with Fig. 143. This leads to cyclohexene rings,

conjugated system activated cyclohexene ring
       double bond
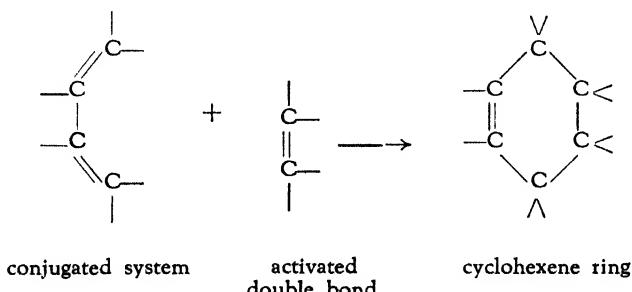
Fig. 143. Principle of the DIELS-ALDER reaction.

[1] C. ELLIS, The Chem. of Synthetic Resins, New York 1935, p. 1215.
[2] C. P. A. KAPPELMEIER, Fettchem. Umschau, 42 (1935) 145.

which also form bridges between the chains. Although in certain cases the carboxyl groups can also react, these are not important initially for the interlinking reactions, in contradistinction to what will be said in the following section about the dicarboxylic acids. Many attempts have been made to utilize these numerous reaction possibilities in technology. The well-known boiling of *standoil* is, in fact, an artificial interference and therefore this substance may be regarded as a modified natural substance.

By oxidation of linseed oil we obtain *linoxin*, the raw material for the manufacture of linoleum. To this end, linseed oil together with a siccative is spread on cloths so that as large a surface as possible is exposed to the action of oxygen (at 50° C = 122° F). The oil trickles continually onto the cloths until a sufficiently thick layer is formed; this process may take months. In all, about 30% oxygen is absorbed and 25% of volatile matter (CO_2, H_2O, acetic acid) is lost.

In another process, air is blown through pre-oxidized linseed oil in the presence of siccatives. This process takes only about 30 hours.

A third method consists in heating linseed oil with PbO at a temperature of more than 250° C (482° F), while air is blown through it. In one day, the mass is gelatinized. This is highly polymerized, whereas the other kinds of linoxin contain more oxidation products.

The linoxin, made according to one of the two first processes is then melted with resins, e.g., with colophony and copal, at temperatures of 150 to 170° C (302—338° F) until an elastic tough gel is formed. This is stored for a few weeks, in which time a ripening process takes place which is principally of a physical nature, because it can be reversed by heating.

The linoleum cement thus formed, or the product oxidized with the aid of PbO, is kneaded on rolls together with ground cork and other filling and colouring matters. It is then calendered into thin layers, which with jute woven on the back side produce the well-known linoleum.

The mixture can also be ground to a powder and pressed in this form on textiles. In this way it is possible to manufacture different designs by placing powders of various colours on the textile next to one another according to the desired pattern.

Like oxygen, *sulphur* can also be added to unsaturated oils and by heating with rape oil or whale oil at 130° C (266° F) *brown factis* is obtained, which is used in the rubber and linoleum industries as a compounding material. *White factis* is manufactured with $SnCl_4$ in the cold; at present there are types on the market which are chlorine-free.

It is also possible to *dehydrate* castor oil and to obtain an oil which, with two conjugated double bonds per fatty acid chain, stands between linseed

oil and wood oil. It therefore shows a drying rate between that of these two oils, which is of great significance in industry. The *synourin oil* and *dienol* thus obtained make elastic and satisfactorily weather-proof films. By further dehydration a wood oil-like product is formed (*trienol*).

In the next section we shall encounter a further important utilization of the monocarboxylic acids in combination with alkyd resins.

§ 54. ALKYD RESINS AND OTHER POLYESTERS[1]

A whole series of synthetic resins are known, which are made by esterification of mono- or di-carboxylic acids with poly-alcohols. Consequently we are concerned here with equilibrium reactions (see p. 7) and according to Kienle (p. 16) we must discriminate sharply between the non-setting and the setting types; for the latter a reaction of a type higher than the (2,2)-type is necessary.

The condensation products of *phthalic acid* anhydride and *maleic acid* anhydride with *glycerine* are very important[2].

phthalic acid anhydride   maleic acid anhydride
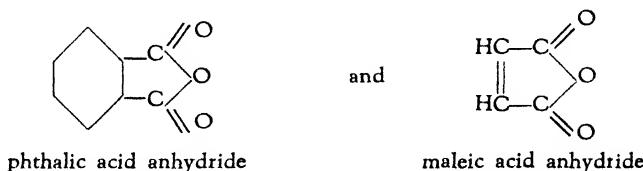
These are both of the (2,3)-type and, therefore, according to the scheme of Fig. 144 can lead to three-dimensional macromolecules.

glycerine   phthalic acid   glyptal resin
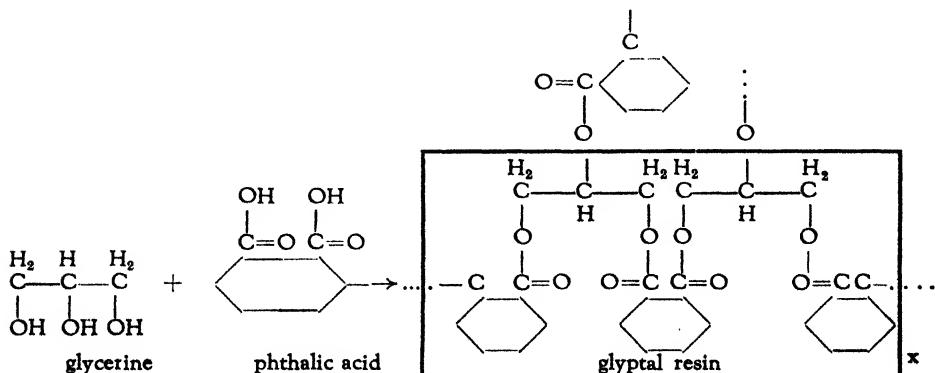
Fig. 144. Formation of glyptal resin.

[1] Compare: H. W. CHATFIELD, *Varnish Constituents*, New York 1944.
[2] Others are: succinic acid, adipic acid, sebacic acid.

Such resins play an important part in the lacquer industry because at low temperatures they remain tough and elastic, adhere well, are clearly transparent, and possess good ageing properties.

With the aid of oleic acids, various combinations can be realized. For the non-drying alkyd resins a combination is formed with non-drying oils, like castor oil or coconut fat. The thick soft resins that form have been generally introduced into the furniture industry as an addition to cellulose lacquers and with urea resins for stoving.

The alkyd resins have found very wide and general applications, from printing inks to fabric coating materials, outdoor paints and baking enamels. Apart from the straight linseed oil paints, they are now the most important of all types of finishes due to their excellent properties combined with a reasonable price (about 15 ℯ per lb). Modified with drying oils they are air-drying, but they can also be used for stoving operations, which is due especially to their weather and gasoline resistance, elasticity, toughness, gloss, and lack of colour.

The modified phthalate- and malenate-resins are manufactured in closed boilers, as shown in Fig. 145, which may have a capacity of up to 1000 litres (250 gal). The manufacturing process is relatively simple, as appears from the flow sheet of Fig. 146. The reaction temperature is high, namely 200—250 °C (390—480 °F). Emulsions are being used more and more for indoor applications. Those rich in oil contain 75 to 80% of oil, others 30 to 40%. The former are used as air-drying, the latter as stoving lacquers. With regard to the maleic acid product we would point out the possibility of the DIELS-ALDER reaction (p. 187). The alkyd resins can also be combined with resin acids and phenol resins (see p. 169-173); in this connection oils can also be used, so that an extensive series of combinations and modifications become possible.

The soft resins thus obtained are dissolved in white spirit and aromatic hydrocarbons (xylene or solvent naphtha), siccatives like cobalt naphthenate are added and mixed on rollers (Fig. 61 p. 89) with pigments and dyes.

The growing importance of alkyd resins may be demonstrated by the fact that in 1943 already 92 million kg of alkyd
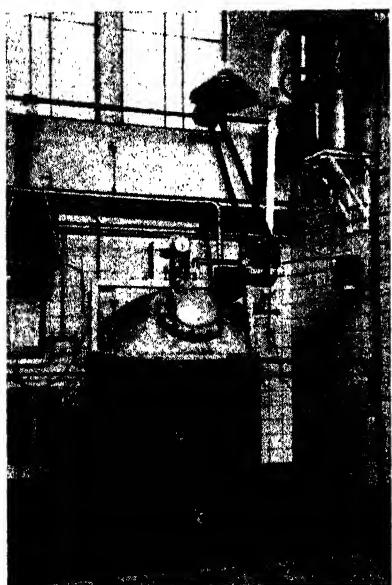
Fig. 145. Installation for the manufacture of lacquer resins.
(Courtesy Sikkens).

resins were used in the U.S.A. as against 180 million kg of pure oil varnishes.

On p. 122 reference was made to the *unsaturated polyesters* made from polyallyl alcohol $CH_2 = CH$. This can react with polybasic acids like maleic

$$\overset{|}{CH_2OH}$$

or phthalic acid giving diallyl maleinate or phthalate. It can also react with
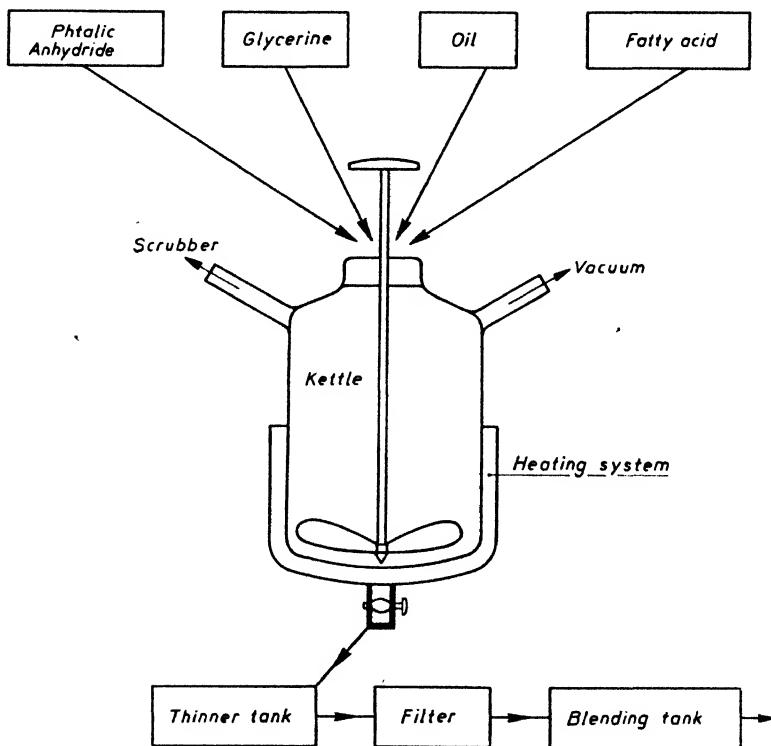
Fig. 146. Flow sheet for alkyd resins.

alcohols, like glycol, leading to ethers. Strictly speaking, the latter do not belong in this chapter, but for convenience we will discuss them together with the allyl esters.

The feature of these materials is that after the condensation between the monomeric alcohol and the acid is finished, a crosslinking can be carried out by means of the allyl double bonds. The advantage is [1] that in the cross-

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[1] *Plastics Catalog,* New York 1945, p. 136.

linking process no water is produced, a point of special importance in making laminates, because in pressing thick pieces considerable trouble is caused in removing water. Especially when applied to glass cloth, which does not absorb any water, the unsaturated polyesters have become popular in low pressure moulding [1] techniques. The hardness and flexural strength of such products are even superior to those made from phenol-formaldehyde resin, notwithstanding the fact that the pressure applied is much lower (see Table 48). Average moulding conditions are 10 min at 150° C (300° F).

Water-white transparent objects can be produced from allyl resins by casting. A disadvantage is the high shrinkage of about 15%. The combination of glass cloth with transparent allyl resins of the same refraction leads to a scratch proof and impact resistant synthetic glass [2].

TABLE 48.

PHYSICAL PROPERTIES OF LOW PRESSURE MOULDED GLASS LAMINATES [3]

Property		Unsaturated polyester resin moulded at 0.04 kg/cm^2 (0.5 lb/inch^2)	Phenolic resin moulded at 1 kg/cm^2 (15 lb/inch^2)
Compressive strength	(kg/cm^2)	3,200	2,100
(edgewise)	(lb/inch^2)	45,000	30,000
Flexural strength	(kg/cm^2)	4,800	3,000
	(lb/inch^2)	67,000	40,000
Water abs. 24 hrs	%	0.5	0.5
Hardness Rockwell M		112	90
Glass content	%	55	45

[1] Modern Plastics, 23 (1946) 144.
[2] Modern Plastics, 25 (1948) 120.
[3] Flastics Catalog, New York 1945, p. 138. See further for the properties of allyl resins: F. STRAIN, Modern Plastics, 21 (1944) 97, 168.

POLYMERS BASED ON CELLULOSE [1]

§ 55. RAW MATERIALS

The structure of cellulose is in the form of molecules consisting of cellobiose units, as shown in Fig. 147. The number of glucose groups per chain is estimated for natural cellulose to be 3000—4000. The chains cannot move
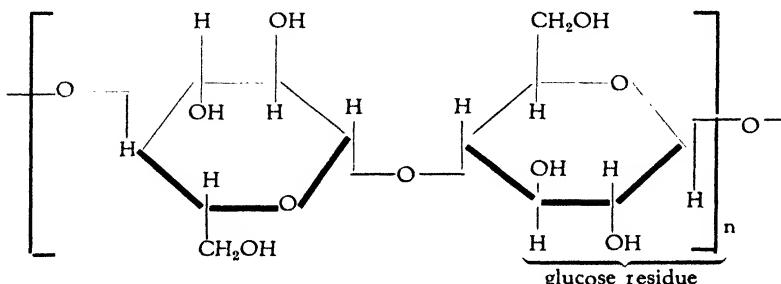
Fig. 147. Cellobiose, the unit of cellulose, consisting of two glucose residues.

freely with regard to each other. Partly they form crystallites (small crystals, crystalline micelles, see p. 30), i.e., lattice domains from which protrude certain molecules like fringes, as shown in Fig. 25 on p. 29. The chains are presumed to be rather rigid, which in combination with the numerous strong dipoles (3 OH groups per glucose unit) explains the tendency to form crystallites. Here lies the key to the manufacture of cellulose plastics, because as long as the firm cohesion in crystallites exists, the cellulose can neither be dissolved nor be plastically deformed. The neutralizing of this cohesion by esterification of the OH-groups destroys the original crystalline pattern, which cannot be restored easily. Consequently, even the case of so-called regenerated cellulose, in which the OH-groups have been regenerated, one

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[1] For general treatments see: E. OTT, *Cellulose and Cellulose Derivatives*, New York 1943.
P. H. HERMANS, *Physics and Chemistry of Cellulose Fibres*, New York-Amsterdam 1949.

is corcerned with materials which are not in every respect identical with natural fibres. This shows itself in the mechanical properties.

The most important sources for cellulose are wood, cotton, and cotton linters (fibres on the cotton seeds); the two latter sources supply the purest form of cellulose. For many technical purposes, however, we depend, as far as prices are concerned, on wood cellulose, especially on that from pine wood, although lately also fir (or leaf) wood and straw is being used. By means of a mixture of calcium bisulphite solution and sulphuric acid, the wood cellulose is degraded by boiling under pressure. During this process the non-cellulose substances are dissolved and the fibrous cellulose mass (the so-called sulphite cellulose) remains behind and is bleached.

We distinguish:

   alpha cellulose, — the part which does not dissolve in 17.5% NaOH and
   hemicellulose, — the part, which dissolves in a NaOH solution of 17.5—
   18 % and which contains the low molecular β-and γ-cellulose.

The ordinary sulphite cellulose contains about 80—90% of alpha cellulose. In recent years, attempts have been made to produce a special kind of cellulose with more than 95% of alpha content.

In cellulose we meet a raw material the composition of which is variable, since not only the alpha content and the composition of its accompanying substances (pentoses) but also the mean chain-length and the proportion of crystalline to amorphous parts can vary.

§ 56. DISSOLUTION AND CHEMICAL MODIFICATION

The presence of numerous strong dipoles (hydrogen bonds between the OH-groups) constitutes the dominating element in industrial difficulty, because for processes like spinning it is necessary to dissolve the cellulose. For the same reason, plastic deformations under pressure are in the case of a strongly cohering material like cellulose possible only to a limited extent. The consequence of this firm cohesion is that only very powerful chemicals are suitable for the dissolution, as a result of which a chain scission often takes place at the same time. For this reason one is often forced to start by chemically changing the cellulose, in order to remove the strong dipoles, e.g., by alkoxylating or by esterification. After carrying out the technical shaping process like spinning, the cellulose is reconverted into its original chemical structure (viscose rayon); the original mutual coherence of the chains is not restored, however, a point discussed earlier.

In general, the derivatives are manufactured according to the scheme of Table 49.

TABLE 49.

SCHEME FOR THE MANUFACTURING OF CELLULOSE DERIVATIVES

(R = cellulose residue).

Examples

Esters
    Cellulose and strong acid

$$CH_3\text{-}\overset{\text{O}}{C}\text{-}O\text{-}R \qquad NO_2\text{-}\ \text{-}R$$

cellulose acetate   celullose nitrate
(Further on propionate, butyrate, etc)

Ethers
    Alkali cellulose and esters of inorganic acids

$CH_3\text{-}O\text{-}R$ $C_2H_5\text{-}O\text{-}R$
methyl ether   ethyl ether

$HOCH_2CH_2\text{-}O\text{-}R$ $C_6H_5CH_2\text{-}O\text{-}R$
hydroxyethyl ether   benzyl ether

Xanthogenate
    Alkali cellulose with NaOH
    and CS_2

$$S=C\text{-}O\text{-}R$$
$$|$$
$$SNa$$
viscose

Cuprammonia silk
    Cellulose and
    $[Cu(NH_3)_4]$ $(OH)_2$ and alkali

$[Cu(NH_3)_4]$ $(OH)_2R$
cuprammonium-silk
solution (secondary
valency bond)

are later re-
converted into
regenerated
cellulose in a
coagulation
bath.

There are two different ways of carrying out the chemical modification.
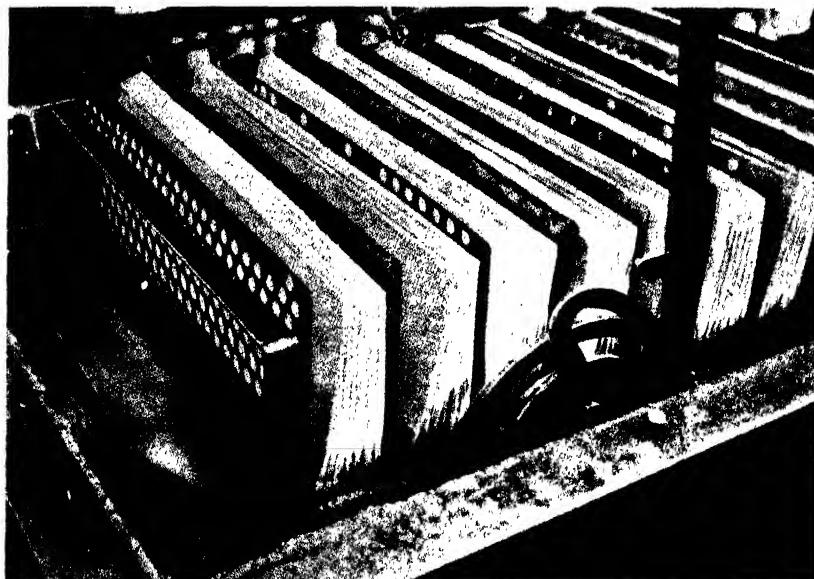
Fig. 148. Soaking of cellulose in NaOH.

One is by first making alkali cellulose, the other is by esterification with strong acids. In the flow sheet of Fig. 151 the processes involved are represented.

a. In the *alkali cellulose* process, sheets of alpha cellulose or cotton linters are swollen in an 18% NaOH solution at 20° C (see Fig. 148). This process, which takes some hours, is called "mercerization". It seems that a well-defined chemical combination is formed so that this process is more than just a swelling. The product thus formed, *alkali cellulose*, is pressed out, the greater part of the soluble hemicellulose being removed. In modern factories the impregnating of the cellulose in endless sheets or in the form of flakes is carried out as a continuous process. In order to render the material more easily accessible to oxygen the alkali cellulose is shredded in a disintegrator (see Fig. 149). By storing during several days [1] at about 25 °C (77° F), the

Fig. 149. Shredder.

so-called *ripening*, a scission of the chains is achieved — as a result of oxidation — which reduces the viscosity in solution. This is just the purpose to be fulfilled because the thick solutions cannot be pumped, making the spinning process impossible. One can distinguish a pre-ripening of the crumbs and an after-ripening of the viscose. Fig. 150 shows [2] that especially during the pre-ripening the greater shortening of the molecules takes

[1] In modern factories this is carried out at a higher temperature in order to speed up the process.
[2] H. SCHWARZ and H. A. WANNOW, *Kolloid-Z.*, 99 (1942) 130.

place. This is explained by assuming that the action of the oxygen on the compact viscose during the after-ripening is less intense than on the more accessible alkali cellulose.

In certain cases (*viscose*) the alkali cellulose as such can be dissolved. It is converted into the *xanthogenate* in kneaders by action of CS_2 in the presence of NaOH.

Fig. 150. Decreasing the polymerization degree of cellulose by the ripening process.

The following reactions thus take place. The alkali cellulose has certain characteristics of an alcoholate; it can react with CS_2 to form an ester of dithiocarbonic acid (xanthogenic acid):

$$NaOR + CS_2 \longrightarrow C\begin{matrix} S\,Na \\ = S \\ O\,R \end{matrix} ,$$

where R = cellulose residue. This ester dissolves in alkali, giving the so-called "viscose" solution. If this is extruded into sulphuric acid, coagulation occurs and cellulose is regenerated:

$$C\begin{matrix} SNa \\ = S \\ OR \end{matrix} + H_2SO_4 \longrightarrow C\begin{matrix} SH \\ = S \\ OR \end{matrix} + NaHSO_4$$

$$C\begin{matrix} SH \\ = S \\ OR \end{matrix} \longrightarrow ROH + CS_2$$
$$\qquad\qquad\quad\; \text{Cellulose}$$
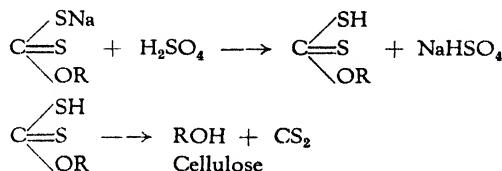
After filtering, the solution is ready for spinning.
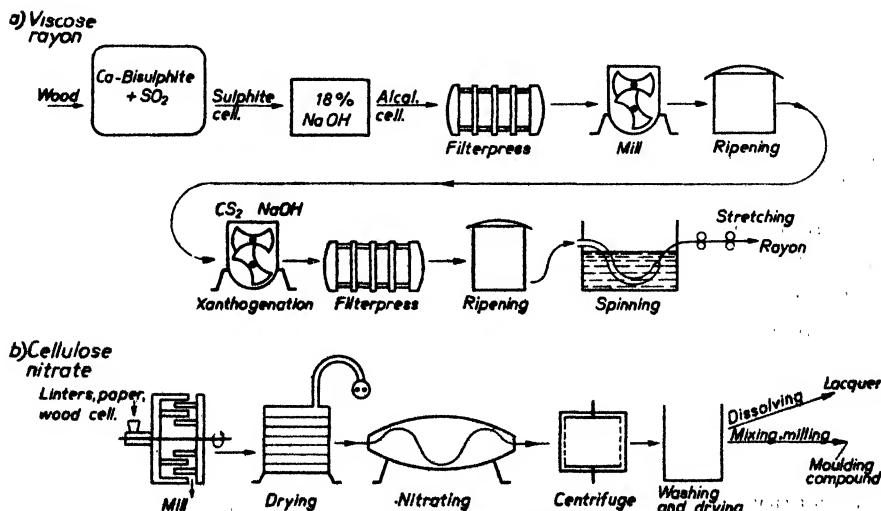
Fig. 151. Flow sheet for viscose rayon and cellulose nitrate as examples of cellulose derivatives.

The degree of xanthogenation is indicated by the number of xanthogenate groups which have been introduced per 100 $C_6H_{10}O_5$-units. Maximally, this number therefore amounts to 300; for the manufacturing of rayon the number of 50 is sufficient. However, during the ripening this number drops to about 35, CS_2 being split off.

b. The *cellulose ethers*, of which the methyl, ethyl and benzyl ethers are the most important representatives, are prepared by action of esters of inorganic acids on alkali cellulose. The etherification is usually effected in autoclaves. The degree of substitution can be regulated at will, which is very important on account of the different solubility of the products thus manufactured.

In other cases, the alkali cellulose is first converted into so-called cellulose hydrate by the action of water. Cellulose hydrate — which is also formed by saponification of cellulose esters — differs from the original cellulose only in that the lattice is deformed, making the material accessible for chemical modification.

c. For the *cuprammonia process*, $CuSO_4$. 3 Cu $(OH)_2$ is dissolved in concentrated ammonia and the cellulose hydrate is impregnated with this solution under addition of alkali. The dissolving process takes place in a few hours; apparenthy during this process the mutually cohering OH groups are separated from each other by the $Cu(OH)_2$. The solution is then filtered and the ripening carried out. In the spinning process the fibre is coagulated in a hot bath (30—40 °C $=$ 86—104 °F), and the cellulose hydrate is regenerated. This cuprammonia method is only occasionally used.

d. In the *esterification* the cellulose is brought into contact with strong acids in the presence of dehydrating agents (H_2SO_4).

Cellulose nitrate, also called nitrocellulose, is obtained by the action of a mixture of H_2SO_4 and HNO_3 on cellulose. By centrifuging and washing the acid is removed and after a stabilizing process the material can be dissolved in esters or other polar solvents. For the manufacture of plastics the nitration is carried on until the nitrogen content is up to 10.5—12.5% (the maximum value is 14.2%), whereby a little more than 2/3 of the OH groups are converted.

Cellulose acetate (acetyl cellulose) is manufactured in a similar manner by the action of acetic anhydride on cellulose in the presence of sulphuric acid.

§ 57. THE MANUFACTURE OF FIBRES, FILMS, AND LACQUERS

As mentioned already, the cellulose solutions are especially suitable for the manufacturing of fibres or, what is actually the same, of films, because

the latter can be regarded as fibres spread out flat. For the manufacture of rayon the spinning solution, in the wet process, is extruded into an acid bath (see Fig. 153), whereby a chemical reaction regenerates the hydroxyl groups of the cellulose in the fibre which is being formed. On the other hand, there is the *dry spinning process*, in which the solution is pressed out into the air, the organic solvent (acetone, alcohol) being evaporated.

We will consider viscose rayon more closely as it is of greater importance. The nozzle represented in Fig. 153 contains 15—150 holes with a diameter between 0.07 and 0.10 mm. The number of holes fixes the number of separate fibres in the rayon thread. Their thickness is determined by the ratio between the quantity of viscose supplied per hole and the extrusion velocity. This thickness is expressed in deniers, by which is meant the weight in grams of a fibre of 9000 meters [1].

The spinning bath (Fig. 154) consists of certain sulphates dissolved in 6—10 % sulphuric acid; for this reason the nozzles are made of precious metals: gold, palladium, platinum.

Considering the spinning process in more detail (Fig. 152), two [2] zones can be distinguished in which the fibre is being formed. The outer skin coming into contact with the precipitating bath will coagulate, while the core still consists of xanthogenate.

Between these two zones there is a transition. It is obvious that, due to this phenomenon, the maximum spinning velocity is connected with the speed of diffusion into the fibre.

As we shall see on page 210 a certain orientation of the molecules is very important for the properties of the artificial silk. For this orientation a special stretching process is applied. The fibres are conducted over a system of cylinders which rotate with a suitable velocity.

Fig. 152. Zones in spun fibres.

According to the manner in which the spun artificial silk is collected, we distinguish two spinning processes. In the *centrifugal- or spinning pot-procedure* the fibre is led from the cylinders into a small, quickly rotating centrifuge

[1] The metric number is found from the equation: metric number $= \dfrac{9000}{\text{denier number}}$

[2] H. L. BREDEE, Chem. *Weekblad* 30 (1933) 51; 34 (1937) 296.

— the spinning-pot — and in this way the so called spinning-cake is formed. The thread is twisted, which is not done in the *bobbin procedure*, where the fibres are wound on a spinning bobbin.

The purification takes place by placing the cakes or bobbins one on top of the other and alternately washing with water, a mixture of Na_2S [1] and bleaching lye and finally a soap solution for finishing. Then the drying, the conditioning (i.e., the adjustment at a certain degree of moisture) and the shipping take place.

For the cuprammonium silk the spinning process is different. It includes, however, only 3% of the world production, and so we shall not enter further into this matter. The acetate silk is manufactured principally according to the dry spinning process.

Fig. 153. Spinning nozzle in the wet spinning procedure (viscose).
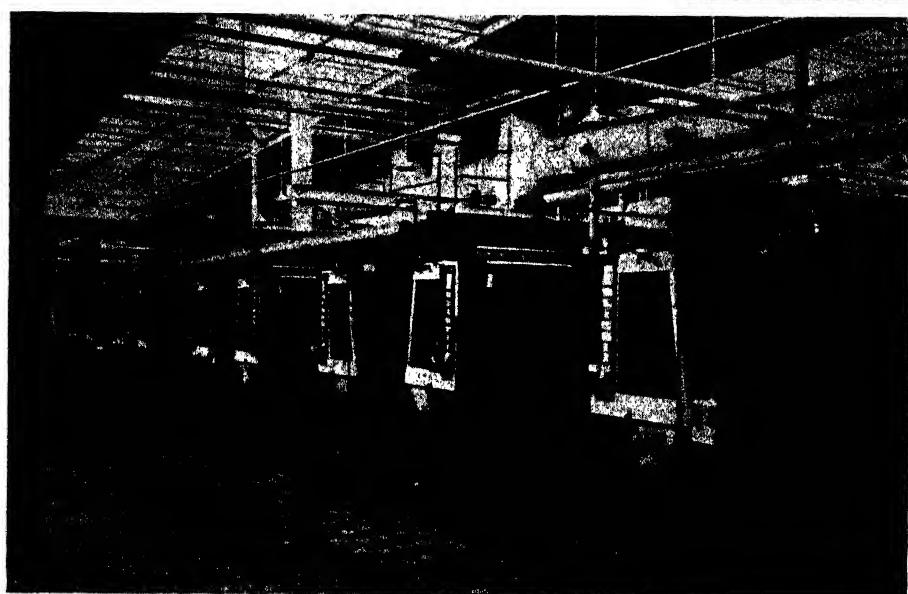
Fig. 154. Spinning bath for viscose filaments.

[1] In order to dissolve sulphur.

Staple fibre is a product of the rayon industry, now occupying about half of the market for artificial textiles. The name staple fibre indicates the manufacturing process. A great number of rayon filaments are assembled into a cable which is cut across. In this way bundles of short fibres with a certain staple length are created which look like cotton, and in a similar manner are spun into threads. The thickness and the staple length of the fibres are varied according to whether these are adapted to the cotton- or the wool-type.

Fig. 155 shows a manufacturing scheme; it should be mentioned that the cutting can also take place after the drying. In order to improve the adhesion

| | Cutting | Drying | Compressing |
| Spinning machine | of the cable | | into bales |
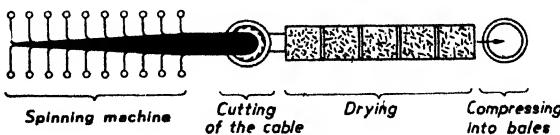
Fig. 155. Scheme of the manufacturing of staple fibre.

after the spinning, an attempt is made to create as raw a surface as possible on the fibres.

It should be remarked that the introduction of staple fibre has even rendered necessary an extra step in the working process, namely, the spinning.

One might therefore ask what the advantages are. These can be found in the fact that many difficulties which existed in the more ancient rayon industry disappear. No high demands need be made on the uniformity of the titre and on the dyeing capacity and therefore cheaper raw materials can be used and the extruding velocity in the spinning process can be increased. Moreover the spun fibres include a lot of air, making the threads better heat insulators; these threads possess a character of their own which creates new aspects for the trade. Generally speaking, it represents, as against rayon filaments, a new textile of great importance, especially for cotton-poor countries. Spun rayon from viscose is by far the most important kind; it is mostly employed as an adjunct to cotton and other fibres. In a free market it is questionable whether staple fibre can ever compete with cotton, which EISENHUT [1] explains as follows. The difficulty in the matter of competition does not in the first place concern the price (see p. 243). However, the difference in wearing quality of, for example, a shirt is from $1/6$ to $1/3$ in favour of cotton and therefore nowadays the competition still fails on account of the difference in quality. This is doubtless the reason, why in the U.S.A. staple fibres are only produced

[1] EISENHUT, *Kolloid-Z.*, **98** (1942) 199.

to an extent of 30% of the amount of rayon, whereas in Germany during the war this percentage was 340 (see Table 60, p. 243).

The manufacturing of *films* shows a great similarity to that of rayon; here
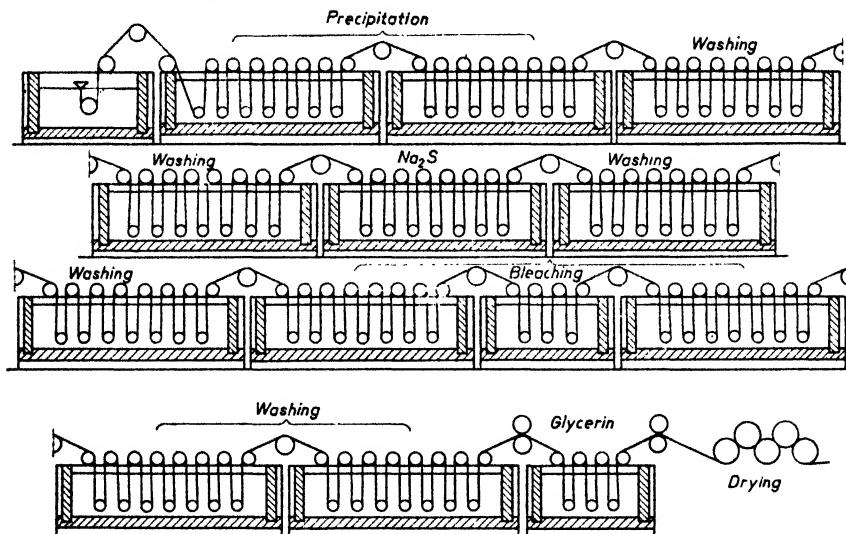
Fig. 156. Film casting-machine.

also we start either from solutions in alkali or in organic solvents. Instead of a spinning nozzle, casting machines are employed which mostly possess

Fig. 157. Manufacturing cellulose xanthogenate films.

an adjustable aperture in the form of a slit. Fig. 156 shows a film casting machine in which cellulose films are manufactured from a xanthogenate solution. We see the slit, the precipitation compartments and next to those the tanks for washing, for bleaching and for doping with glycerine (in order to soften the material)· Fig. 157 shows the film passing through the bath.

Machines of a different type have rotary drums on which the film is poured out. The drum then conducts the film into the coagulation bath and, after stripping off, it is lead away for further treatment.

The films manufactured using organic solvents, in which case the coagulation is left out, are usually also obtained by pouring the mass onto a cylinder or an endless band. The solvent is evaporated by heating, and after complete drying the film can be wound up. Cinema films, especially those made from acetyl-cellulose, have come to the fore on account of their non-inflammability. At present, ethyl- and benzyl-cellulose films are used for wrapping purposes due to their low moisture permeability.

Another application is that of *dipping*; this method was already indicated on p. 91. It is specially applied in the case of acetyl-cellulose.

The dipped articles may be regarded as kinds of lacquered (varnished) objects which show something special only in that the coating is afterwards separated from its base. In this way we automatically enter the domain of the *lacquers*. As in rayon manufacture the lacquers are also applied in aqueous solution as well as in organic solvents, but here the latter play the principal part.

It is interesting to note that here also the problem of dissolution is decisive for the possibility of application. About 20 years ago the cellulose lacquers had not yet obtained important markets, because it was not possible to manufacture solutions with a sufficiently low viscosity. Or to put it more correctly, a low viscosity could be realized, but the dilution had to be so great that an extraordinary waste of solvents took place, so that there was no practical utilization. Only after it was possible to shorten the cellulose molecules by means of oxidation (ripening) solutions with a practically usable viscosity coupled with a sufficiently high cellulose content could be made (see p. 68 regarding the connection between viscosity and molecule length). Since that time the spraying- and dipping-lacquers have been made use of on a large scale. Especially the nitrates and the acetates have come to the fore in this connection, moreover, the methyl, the benzyl and the ethyl ether must be considered. Mixed derivatives like acetate-butyrate have become popular since they are soluble in a wider range of solvents and are compatible with a greater number of plasticizers and other polymers. A further point is that these films have a very good adhesion.

Lacquers made from cellulose derivatives are used in practice with addi-

tions, for otherwise the film would be too brittle and would have too little adhesion. Various resins have gained great importance as fillers, and have the additional advantage that the concentration can be considerably increased, maintaining a certain viscosity as the resin molecules are globular (cf. p. 57). As plasticizers, various substances like tricresyl-phosphate are used; moreover, dyes, pigments, etc. are added.

The choice of the solvent is extremely important, for on one hand the price is influenced and on the other hand important properties, such as the drying rate are connected with it. We distinguish *active* solvents which by themselves are capable of dissolving the cellulose derivative, and also *diluents* which themselves are not solvents but are added for reasons of cost or to influence the rate of vaporization. We also distinguish the solvents according to their boiling points; low boiling points increase the drying rate; solvents of high boiling points are often specially added to improve the flowing capacity of the lacquers. An average nitrocellulose lacquer contains 55—60% of low, 35—45% of medium (110—130° C.) and 5% of high boiling solvent.

In contrast to oil lacquers, the drying is only based on evaporation and not on oxidation or interlinking, i.e., on a physical process which is very rapid. The cellulose lacquers have brought considerable progress especially as regards the automobile and aeroplane industries because they make possible a quick drying, which is indispensable for mass production.

When we considered above lacquers in aqueous solution, we meant the *lacquer emulsions* which have come to the fore especially in the recent years, because they need no organic solvents. A further advantage of these emulsions lies in their low viscosity, so that a layer with a great macromolecule content can be applied by spraying or dipping in one operation.

Special applications of solutions based on cellulose derivatives are found in artificial leather and in textile finishings. Artificial leather is manufactured by coating a certain under-layer, like a fibre band or a tissue impregnated with rubber latex, with a lacquer (see scheme of Fig. 63d, p. 91) and afterwards pressing in a grain by means of engraved rolls. For this coating the different cellulose derivatives are suitable; they compete with natural rubber latex and with vinyl derivatives. Often combinations of the different kinds are employed, e.g., a vinyl resin layer is used as a layer between the rubber and the cellulose lacquer. Textile finishes can also be applied by means of the coating process. By employing alkali soluble cellulose ethers, like hydroxyethyl cellulose and methyl cellulose, wash proof finishes can be obtained.

§ 58. THE MANUFACTURE OF MOULDED PRODUCTS

The oldest material known for the manufacture of moulded products is *celluloid* [1], a mixture of cellulose nitrate and camphor. Both ingredients are mixed together in a kneader with the addition of alcohol as a solvent. After the ductile mass has been pressed through a sieve for cleaning, the greater part of the alcohol is removed in a vacuum and the compound is then masticated on rolls (see p. 90). The material is pressed into blocks and sheets are cut from these. The last traces of alcohol are removed from these sheets in a drying oven and in order to obtain a high lustre the sheets can be pressed between polished nickel-plated steel sheets (Fig. 158). If rods or tubes are needed instead of sheets, these can be manufactured in an extrusion machine (p. 94).

The cellulose nitrate renders the celluloid highly inflammable; the material is so easily distorted that it cannot be used in the injection moulding process and for this reason cellulose acetate is often used in its stead. In the latter case, however, plasticizers must be incorporated; diethyl phthalate, dimethyl phthalate and triphenyl phosphate are important in this respect. Additions of 20 to 35 per cent are usual.

Fig. 158. In order to achieve high lustre celluloid plates are pressed between polished nickeled plates.

In fig. 93c it was shown how, by means of the drawing and blowing method, shaped articles and hollow pieces can be manufactured in a simple manner out of flat sheets. Celluloid is very suitable for this process.

However, the manufacture of injection *moulded products* (see p. 110) has become much more important, and cellulose acetate is particularly suitable for this.

By adding plasticizers, filling materials and dyes, mixtures with varying properties can be manufactured by similar methods as are used for celluloid. After grinding in a high speed mill a granular moulding powder is obtained.

[1] See: Plastics Monograph No. 7, Inst. of Plast. Ind., London 1947.

Fig. 159 shows some products manufactured from acetylcellulose in this way. They are not inflammable and the products have a hard, smooth surface.
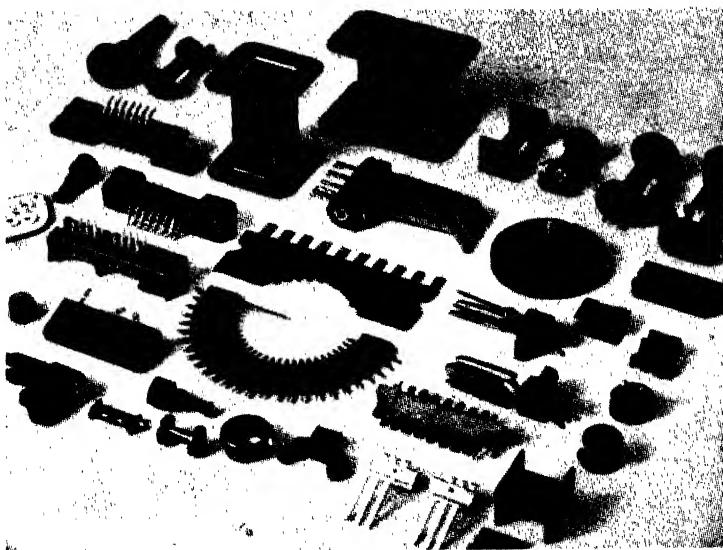
Fig. 159. Injection moulded products manufactured from cellulose acetate.

The toughness is also a very favourable factor for thin-walled products, as is indicated by the impact resistance of 2.4 ft lb/in. Notwithstanding this high value, plasticized cellulose nitrate is still more resistant to impact (4.5 ft. lb/in), but the fact that it cannot be injection moulded hampers its application for many purposes (high quality goggles). It seems that the propionate and the acetate-butyrate will be the solution, offering the combination of a high impact resistance and the ability to be injection moulded.

The development of better machines for injection moulding has in recent years considerably increased the ability of the cellulose derivatives to compete with the phenol-formaldehyde compression moulding compounds. Generally speaking, moulded products with a smaller volume than 10 cm^3 can be manufactured more cheaply from cellulose derivatives. For bigger pieces the cost of the material is relatively more important, so that in general phenol-formaldehyde materials turn out to be cheaper. In this comparison the technical properties have been left out of consideration. It is not surprising that in the case of a thermoplast like cellulose acetate the heat distortion temperature is only 70° C (160° F). On the other hand, the considerable impact resistance is one advantage of this type of materials. In later years some ethylene derivatives, especially polystyrene (p. 110), have begun to compete with cellulose acetate for injection moulding purposes. The price

to be expected in the future for polystyrene (see page 246) will make this competition still greater. Furthermore, polystyrene has the advantage of possessing better electrical properties, a greater chemical resistance and a lower specific gravity. It is inferior with regard to the impact strength.

§ 59. OTHER APPLICATIONS

Besides those mentioned already, there exist other applications, of which we will mention only a few.

If a ring-shaped nozzle is used for the manufacturing of films (p. 157), thin tubes are obtained which can be used as *artificial guts.*

Artificial sponges can be made from a viscose solution mixed with a salt like $(NH_4)_2SO_4$ by heating it in an autoclave at 180° C (356° F) for a few hours. The salt brings about the formation of pores; fibres can be added for stiffening.

Methyl cellulose, being water-soluble and giving viscous solutions, is used as a thickening agent in the textile and in the adhesives industry. Being edible, it is used as a base for thickening food products (salad dressings).

Oxidized cellulose, in which the OH groups have been partly converted into COOH groups, is an acid soluble in weakly alkaline solutions. It is used as surgical bandages, where use is made of its solubility in the alkaline fluids of the body.

Vulcanized fibre stands a little apart from the other cellulose derivatives, but will be discussed here nevertheless. When cotton rag paper, capable of absorption, is dipped in a warm $ZnCl_2$-solution, the material starts swelling, which causes the individual paper-fibres to adhere to each other, thus forming a homogeneous mass. After washing, an extraordinarily tough material is obtained with an impact strength of about 6 ft lb/in. It can be readily machined and post-formed. It was very favourably received in the trunk industry. Up to 5 cm thick plates can be manufactured, which, however, have the disadvantage that the extraction of the zinc chloride takes at least one year. Instead of sheets, tubes can be manufactured by means of a wrapping machine. In recent years the properties have been considerably improved, e.g., by impregnating with artificial resins, water-repelling agents, etc.

§ 60. PROPERTIES OF THE FINISHED PRODUCTS

Generally speaking, fibres made from cellulose derivatives possess reasonable properties, compared with other textiles. It appears from Fig. 160 that the stress-strain curve can be of the same type as that of stiff fibres like ramie and cotton. It can, however, also compare with soft fibres like hair or wool. This depends on the degree of stretching, a point which has been discussed in detail on p. 45.
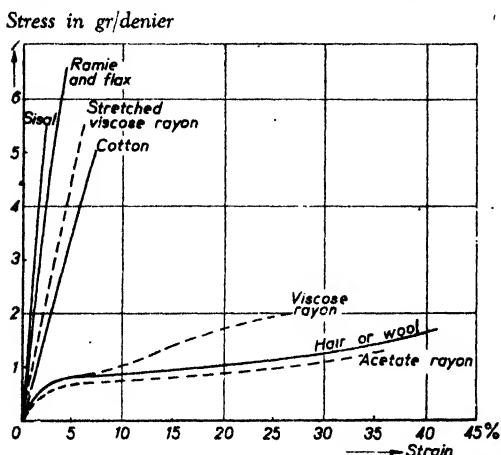
Fig. 160. Stress-strain curves of some kinds of rayon compared with natural fibres [1], [2].

The good stress-strain properties are due to the considerable molecular length and to the large secondary cohesion forces due to the strong dipoles (OH groups). For this reason, cellulose is one of the chief building elements in nature; in technology, rayon, cellophane films, and moulded pieces have been favourably received because of their excellent strength.

However, not only the stress-strain curve describes the mechanical properties of a material, especially when it is to be used as a textile. Perhaps still more interesting is the elastic recovery after deformation, because this determines the property of creasability. In this respect, the cellulose derivatives are rather poor, a point which will be discussed on p. 220 in comparison with other fibres.

It is interesting to note that, in automobile tyres, cords made of highly oriented viscose fibres have replaced cotton for a great part, due to a greater strength under hot conditions.

The properties of the cellulose derivatives are determined principally by three factors:

a. the molecular length

b. the molecular orientation

c. the character of the side groups (substituents).

[1] R. MEREDITH, *Shirley Institute Memoirs*, 19, July 1944.
[2] A stress of p gr/den is equal to 900 p d kg/cm², where d = spec. gravity.

These factors exercise an influence on fibres as well as on films and also on thick-walled products; therefore we shall discuss them in detail.

a. *The molecular length.* The research carried out by STAUDINGER in particular has shown that not only the viscosity in solution (p. 55) but also the mechanical properties in the solid state depend on the molecular length, see Fig. 30a, p. 35. In this connection, it might be asked why the ripening method was introduced, resulting in decreasing the strength. The answer is that the less viscous solutions are needed, as otherwise operations in the manufacturing process like spinning or moulding would be too difficult to be carried out.

Table 50 shows the average molecular weights for some cellulose derivatives as encountered in practice. It appears from these data that it is customary to adjust the molecular length to a large extent to the exigencies of practice.

TABLE 50.

AVERAGE MOLECULAR WEIGHT OF SOME CELLULOSE DERIVATIVES [1]

	Average mol. weight
Native cellulose (cotton, ramie, wood)	2500
Cellulose in bleached cotton linters	1300
Cellulose in purified wood pulp	1000
Regenerated cellulose in rayon	450
Regenerated cellulose in cellophane	350
Nitrocellulose for moulding	2000
Nitrocellulose for extrusion	1000
Nitrocellulose for coatings	300
Cellulose acetate for coatings	300
Methylcellulose	400
Benzylcellulose	125

As appears from Fig. 30, p. 55, it would in practice be useless to aim at a degree of polymerization higher than about 1500, as the properties regarding strength cannot be further improved in this way. However, as moisture decreases the secondary cohesion, it is desirable to keep the molecular length as great as possible in order to obtain rayon with a high strength under wet conditions.

From Table 51 we see that conclusions concerning the connection between degree of polymerization and strength also concern the derivatives.

Besides the molecular length, the dimensions of the crystallites are also of great importance regarding the mechanical properties. However, we cannot enter further into this matter.

[1] Partly after H. MARK, *Am. Scientist*, 31 (1943) 104.

TABLE 51.

INCREASE OF THE MECHANICAL PROPERTIES OF A CELLULOSE NITRATE
FILM WITH THE DEGREE OF POLYMERIZATION (FILM THICKNESS 0.080 mm; 12% N).

Average degree of polymerization	Tensile strength kg/mm^2	Extension at rupture %	Flex test number *
42	8.9	5	25
57	9.8	8	69
65	10.1	10	92
114	10.8	19	151
179	11.2	22	243
269	12.4	23	262
372	13.2	24	206

* Number of times that a strip can be folded without breaking.

b. *Molecular arrangement.* As explained already on p. 34, the strength of materials with chain molecules depends greatly on the degree of orientation. Especially in the case of films and fibres, advantage has been taken of this knowledge by subjecting these substances to a stretching process. Fig. 161 shows the improvements which can thus be achieved. A better degree of orientation gives a higher tensile strength but diminishes the elongation at rupture. Practice has proved, however, that a too great orientation is not desirable, as in that way the rayon becomes too creasable. The moisture
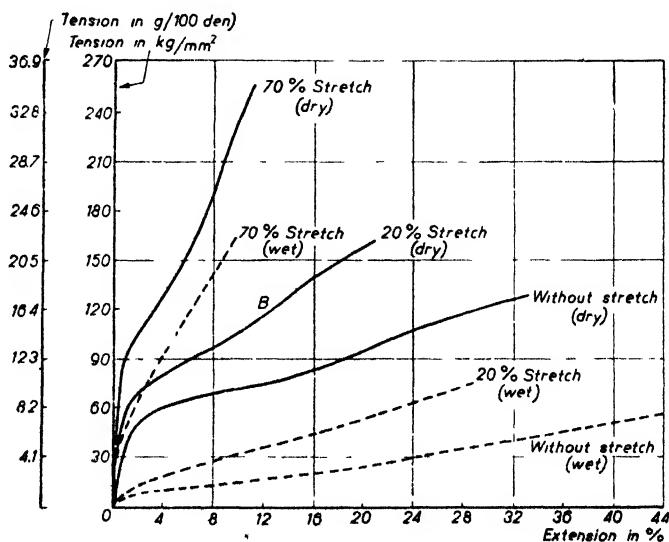
Fig. 161. Dependence of the mechanical properties of rayon on the degree of orientation (example, viscose).

resistance generally increases by a more complete orientation. This is probably

connected with an increase in the crystallization. Industry is now able, by regulating the degree of orientation exactly, to adapt itself to the requirements of practice. It is very doubful, however, whether the same arrangement existing in the original natural cellulose can ever be restored (see p. 16) and therefore it can be predicted that artificial silk will always remain a material different from natural cellulose products.

c. *Character of the side groups (substituents)*. In the light of our detailed discussion on p. 00 regarding the influence of the secondary bonds on the properties of a material, it will be readily understood that when strong dipoles like the OH groups of the cellulose molecule are replaced by others, the properties of the material must be modified considerably.

This is the reason why we find such a large series of derivatives. Of great importance is the work by HAGEDORN AND MOELLER [1], who have systematically examined the variations in the *tensile strength* dependent on the length of the side chains. Fig. 162 shows that the result is confirmed exactly by the findings established according to Fig. 82, p. 118, with regard to acrylic esters [2]. The secondary cohesion decreases as the length of the side chains grows.

The etherification of the OH groups can be conceived in a certain sense as a kind of internal softening (see page 59) because the cellulose units acquire a greater mobility as the substitution of the OH groups proceeds. This is demonstrated by the finding [3] that by the introduction of three acetate groups (i.e., by complete acetylation) the brittle temperature of the hydrate cellulose of 62 °C drops by 13 °C. However, it was also found that here the external softening is much more effective; in the case of the acetylcellulose, e.g., 5% of tricresyl phosphate is sufficient to decrease the brittle temperature by 130° C.

Fig. 162. Decrease of strength for cellulose derivatives with increasing length of the side chains.

Above, it was mentioned how the impact strength largely depends on the type of side groups. The nitrate is brittle, the acetate, the propionate, the acetate-butyrate and the ethyl-ether are tough.

[1] M. HAGEDORN and P. MOELLER, *Cellulosechemie*, 12 (1931) 29.
[2] What is found for the acrylic esters in the weakening temperature is found for the cellulose derivatives in the tensile strength.
[3] K. UEBERREITER, *Z. physik. Chem.*, B 48 (1941) 197.

As is obvious, the *chemical resistance* is dependent on the composition of the side groups, and by the way in which these are attached to the cellulose base molecule. To give an example of the last mentioned fact, it may be mentioned that ethylcellulose is more alkali-resistant than the esters due to its ether linkage.

Also, the *sensitivity to solvents* depends, in the first place, on the character of the substituents (see p. 52). Viscose with its three OH groups per glucose residue swells very strongly in water; sodium carboxymethylcellulose is even soluble in hot or cold water. Due to the combination of polar and non-polar groups, it is used as an emulsifying agent.

Benzylcellulose with three benzene nuclei instead of the hydrophilic OH-groups repels water; it is one of the extremes of the hydrophobic types and is soluble in non-polar hydrocarbons.

In the case of rayon, the sensitivity to moisture is important in view of the strength under wet conditions. For foils and lacquer films it is a dominating factor regarding their use as a packing material. Viscose films are often improved, not by substitution, but by covering them with nitrocellulose lacquers. In this way the permeability to water-vapour can be easily reduced to one tenth by means of a layer 0.5 to 1.0 micron thick.

The *electrical properties* — as in the case of the majority of organic materials — run parallel with the moisture sensitivity. For this reason, ethyl- and benzyl-cellulose are excellent insulating materials (great specific resistance), showing, moreover, small dielectric losses on account of their non-polar side groups. Nitrocellulose and cellulose acetate are fairly good insulators provided they are sufficiently highly substituted, but in an alternating current they are less suitable due to the polarity of the substituents. Table 52, in which vulcan-fibre is also included as an example of a bad insulator, shows the difference with the less polar benzylcellulose. The low heat resistance (about 70° C) is one of the weakest points of all cellulose insulators and is, of course, connected with their chain structure. They are typical thermoplastics. For further details, cf. Table 25, p. 82 and 84.

TABLE 52.

ELECTRICAL PROPERTIES OF SOME CELLULOSE DERIVATIVES

	Specific resistance in Ω . cm	Dielectric losses tg δ (at 800 Hz) in 10^{-4}
Cellulose acetate	10^{12}	300
Nitrocellulose	10^{11}	—
Benzylcellulose	10^{15}	50
Vulcanfibre	10^{6}	800

CHAPTER XII

POLYMERS BASED ON PROTEINS

The most important polymer based on protein is hardened casein in the form of artificial horn or artificial wool. Efforts have also been made during recent years to utilize other proteins as raw materials. Moreover, entirely synthetic proteins, the so-called superpolyamides, have been developed recently and are now produced on a large scale (Nylon).

§ 61. RAW MATERIALS

Casein is a protein with a molecular weight of 375,000, each molecule containing more than 200 structural units. There is evidence that the molecule

$$H_2N \ldots \ldots - CO - NH\text{-}CH - \ldots \ldots COOH$$

with R_1 above the CH, and "structural unit" bracketing CO — NH-CH
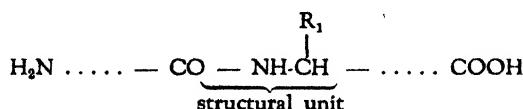
Fig. 163. Probable structure of casein (R = side chain).

has the structure shown in Fig. 163, but it is possible that the grouping of the various units in the molecule differs from case to case. A small quantity of phosphorus and of sulphur seems to be present in the side chains.

The casein is obtained from skim milk (milk contains 3% of casein) by coagulation with the enzyme rennet; it is dried and then supplied to the industry in the form of coarse flakes.

For the manufacture of superpolyamides, diamines and dicarboxylic acids are utilized, both with at least 4 methyl groups. Suitable diamines are tetra-methylene-, pentamethylene-, hexamethylene- and decamethylene-diamine; suitable dicarboxylic acids are adipic, pimelic, cork and sebacic acid. Diamines and dicarboxylic acids with hydrocarbon chains containing less than 4 methyl groups have, up till now, been without practical interest for the manufacture of polyamide polymers.

§ 62. CASEIN PLASTOMERS[1]

In order to incorporate foreign ingredients into casein, it must first be rendered plastic. For this purpose it is moistened with water and the gel thus formed can be easily mixed with the necessary fillers, pigments, dyes, plasticizers, etc. (see Fig. 164). Then the plastic material is forced through an extruder, as shown in Fig. 166, in which some very important processes take place. The spindle presses the casein at 50° C (122° F) through a sieve; the ensuing resistance causes a pressing and kneading action which renders the casein more homogeneous, more plastic and also more condensed. The jet, which in consequence of its water content is in a soft condition, is orientated in the mouth piece, which causes a considerable increase in density. In the machine direction, a strength 5 to 6 times greater than in the perpendicular direction is found. The increase in density is one of the essential conditions for achieving good mechanical properties in the final products.

Rods can be manufactured in this extrusion machine. For the manufacture of sheets the rods are placed in frames and hot moulded in multiple daylight presses. It is here that the conversion of the casein into the final state takes

Fig. 164. The mixing of casein with the other ingredients.

place, namely by hardening with a 5% formaldehyde solution. Chemically, the reaction can perhaps be understood through the scheme of Fig. 165. The interlinking of the molecules by the —CH_2— bridges explains why the material

$$\overset{|}{N}H + CH_2O + \overset{|}{N}H \; \rightarrow \; \overset{|}{N} - CH_2 - \overset{|}{N} + H_2O$$
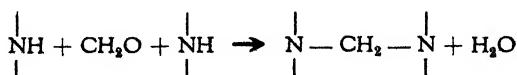
Fig. 165. Probable chemical process during the hardening of casein [2].

becomes harder and less capable of swelling. The process is effected in large baths (Fig. 167). It takes a long time because the aldehyde must enter into the interior of the material by diffusion. The duration increases with the second power of the thickness of the material and for thick plates is as much as a year.

In Fig. 168 the rate of binding between ground acid casein and formalde-
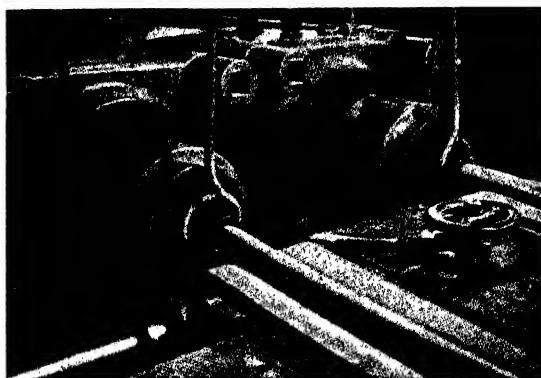
Fig. 166. Extruder for the plasticizing and compression of casein.

Fig. 167. Hardening baths for casein.

hyde is shown [1]. The maximum amount of formaldehyde bound by 1 g of casein is 29.10^{-4} mole. This is 30% more than would be expected assuming

[1] D. C. CARPENTER and P. E. LOVELACE, *Ind. Eng. Chem., Ind. Ed.*, **34** (1942) 759. In these experiments pH = 4.6; the casein is ground to a particle size of 20—40 mesh and the formaldehyde conc. is 6.5 percent. See *ibid.*, **36** (1944) 680 for the influence of concentration on the hardening.

a combination of CH_2O with the NH_2 groups. Further combinations like the formation of acetals and hemi-acetals are thought to take place. It seems possible to reduce the hardening time to one half or to one third by adding swelling agents like KCNS or zinc salt solutions.

After the hardening the product is dried and here also the speed of drying is governed by the diffusion rate. It can be increased somewhat by heating, but there is a limit to this because strains may develop, leading to the formation of cracks.

gr formald bound
per gr casein
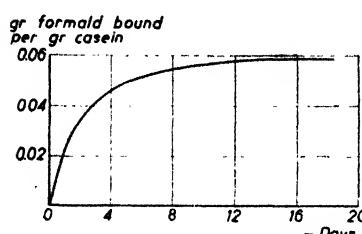
Fig. 168. Binding of formaldehyde by casein.

The process of production is represented schematically in Fig. 169. The majority of casein plastics are manufactured by machining from rods or sheets, because the mouldability is less than might be expected from the low heat resistance of 55° C (131° F). More or less flat work pieces can be shaped by means of the drawing process (Fig. 64c, p. 93), but in deep drawing it is difficult to maintain a good cohesion in the material. Artificial horn has a high impact strength (Izod 1.0 ft.lb/in), but a specific resistance of only 2 megohm cm. Consequently it is a thermoplast of great mechanical strength, which, however, is less suitable for electrical purposes and is difficult to mould.
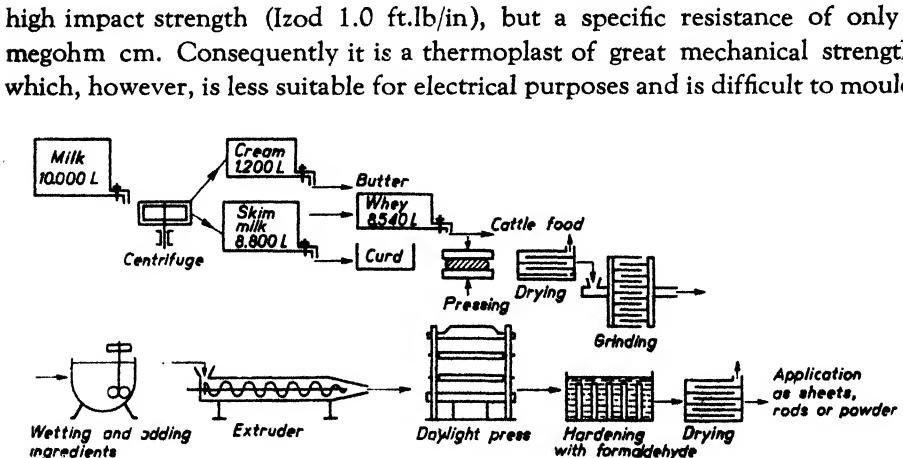
Fig. 169. Flow sheet for the production of artificial horn.

All these properties can be understood by considering hardened casein as a network of polar chain molecules with an intermediate degree of interlinking [1]. If the coherence were based on secondary bonds only, the cohesion in the material should be maintained in the forming process. The broken primary bonds, however, need a large activation energy to be restored, larger than can be supplied by the kinetic energy at the moulding temperature.

[1] Perhaps part of the CH_2-bridges are not formed between two different molecules, but are used in interlinking groups of one and the same molecule (intramolecular ring closure).

The low heat resistance is a proof that only a few primary bonds are present.

Artificial horn is usually used for household purposes and fancy articles; its success is due specially to its bright glossy surface and beautiful tints. Casein still finds application as an adhesive, but for the manufacturing of plywood it is being replaced more and more by urea and melamine resins (see Chap. 8 and 9).

Attempts are also being made to develop other types like soybean, corn and peanut protein as plastics [1].

§ 63. CASEIN FIBRES

This product was first brought on the market by the Italians under the name of *Lanital* (Lana Italiana = Italian wool). Unlike artificial horn, it is not made from rennet casein, but from casein dissolved in NaOH and coagulated with sulphuric acid. As in the case of rayon, the solution is subjected to a ripening process. This being finished, the solution is forced through a nozzle into an acid precipitant. At the same time the fibres are subjected to an orientation process and assembled into a cable. The hardening takes place as an after-treatment by dipping the material in a bath of formaldehyde. It is then washed and dried and the fibres dyed.

The stress-strain curve of casein wool shows a great similarity with that of natural wool; the material fails, however, with regard to strength in the wet condition and elastic recovery (see Fig. 175b), so that it must still be considered as a poor substitute with a great creasability. A favourable circumstance is that it is mothproof.

It is usually used in the form of staple fibre added to natural wool. Its sale will always remain limited on account of the raw material situation. In 1944 the total production in U.S.A. was 5,000 tons p.a. Other proteins are also being tried as raw materials for artificial wool. From egg albumin and chicken feather keratin, fibres of a strength comparable to that of rayon (of the order of 3,500 kg/cm^2 = 50,000 p s i) can be produced [2]. With peanut protein a tensile strength of 1,000 kg/cm^2 (15,000 p s i) and an extension at break of 80% can be obtained; with soybean fibre a strength of 65% of dry wool and of 25% of wet wool [3].

The reason for the difference in properties compared with wool may perhaps be due to the fact that in wool the regularly arranged polypeptide chains can be coiled and uncoiled, whereas in the other proteins the randomly oriented

[1] *Chemistry and Industry* (1945) 58.
[2] H. LUNDGREN and R. A. O. CONNELL, *Ind. Eng. Chem., Ind. Ed.*, 36 (1944) 370.
[3] *Plastics Catalog*, New York 1945, p. 1042.

chains uncoil only partly. Recently, acetylated casein fibres (Aralac) which have an improved acid resistance have been put on the market.

§ 64. SYNTHETIC POLYAMIDES

We owe to CAROTHERS [1] the development of a group of high polymers, which on account of their constitution can be regarded as a kind of synthetic protein.

They are made by condensation between dicarboxylic acids and diamines, each possessing between 4 and 6 CH_2-groups. According to these numbers (in Fig. 170 indicated by x and y) one speaks of 4,6-Nylon, 6,6-Nylon, etc.

$$\ldots.-HN-(CH_2)x-NH-CO-(CH_2)y-CO-NH-(CH_2)x-NH-CO-(CH_2)y-CO-.\ldots$$
$$\ldots.-HN-(CH_2)x-CO-NH-(CH_2)x-CO-NH-(CH_2)x-CO-NH-(CH_2)x-CO-.\ldots$$
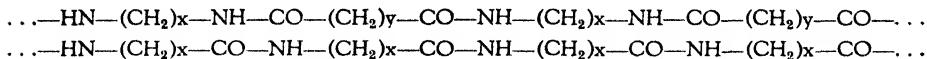
Fig. 170. Two formulae for polyamides.

Here the fundamental structural unit of the natural proteins — CO — NH — — CH_2 — is found. These substances are therefore designated as synthetic polyamides or superpolyamides; the representatives manufactured by DUPONT are well known under the name of Nylon.

The making of Nylon involves [2] three stages as follows:

a. "Nylon salt" is made from a mixture of adipic acid and hexamethylene tetramine in equimolecular quantities, according to the reactions in Figure 171.
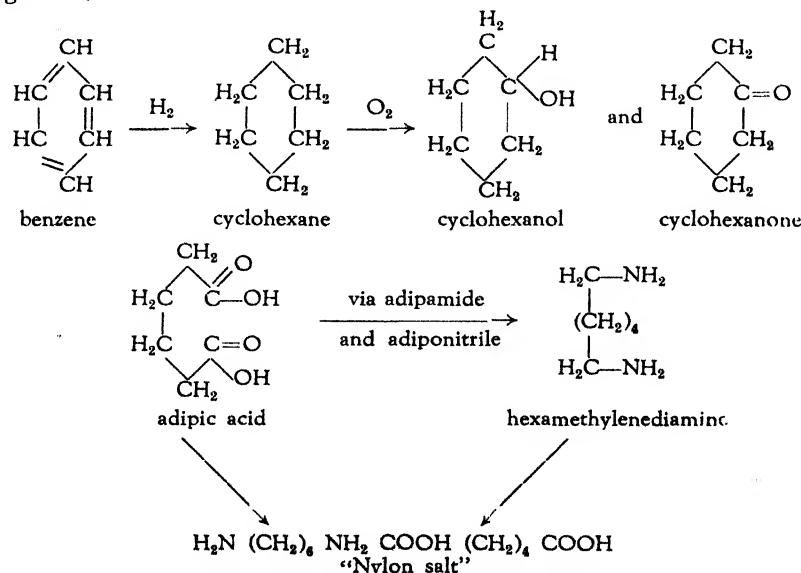
Fig. 171. Formation of "Nylon salt".

[1] W. H. CAROTHERS, Collected Papers, New York 1940.
[2] H. C. MERSEREAU. Chem. Trade J., Febr. 1946.

b. The Nylon salt is heated in a reactor and dissociates into its components; then the polymerization is carried through, in which process the water must be evaporated by vacuum. The polymer obtained is extruded as a ribbon onto a chilled roll and cut into flakes.
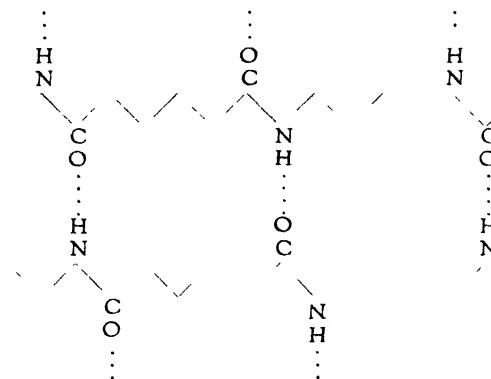
Fig. 172. Lattice of Nylon.

c. The flakes are melted at about 225° C (= 437° F) in a nitrogen atmosphere and spun through a nozzle with a speed of about 10 meters per second (2000 ft per min) and stretched 350 to 450 per cent in order to produce the desired degree of orientation. In this process the CO and NH groups have the opportunity to arrange themselves in the crystalline lattice according to Figure 172. It is this ideal way of crystallization which is responsible for the excellent mechanical properties of Nylon, and as the molecular weight is rather low (7000—20,000), the material possesses very little strength in the non-orientated condition. In order to spin polyamides from a solution, attempts have been made to modify the constitution of the molecule in order to avoid the use of unusual solvents like phenol and concentrated acetic acid.
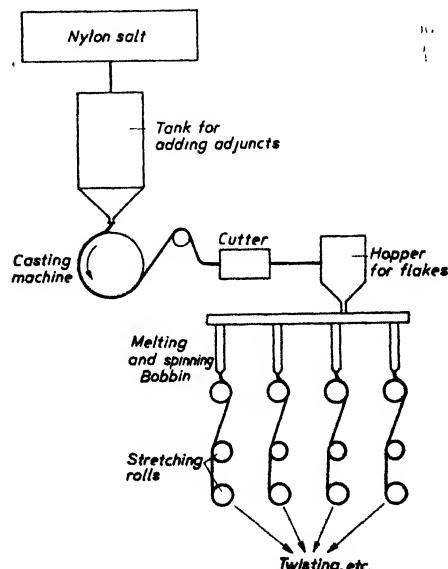
Fig. 173. Flow sheet for Nylon.

Fig. 173 presents a flow sheet for this manufacturing process, which is very complicated in practice, since all parts of the equipment must be kept above the melting point of the polymer and be surrounded by an atmosphere of inert gas.
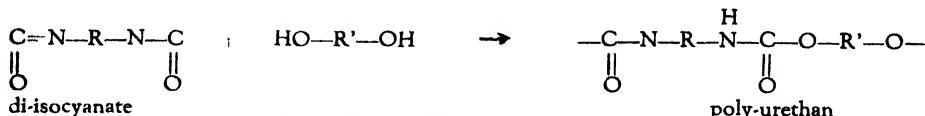
Fig. 174. Formation of poly-urethans.
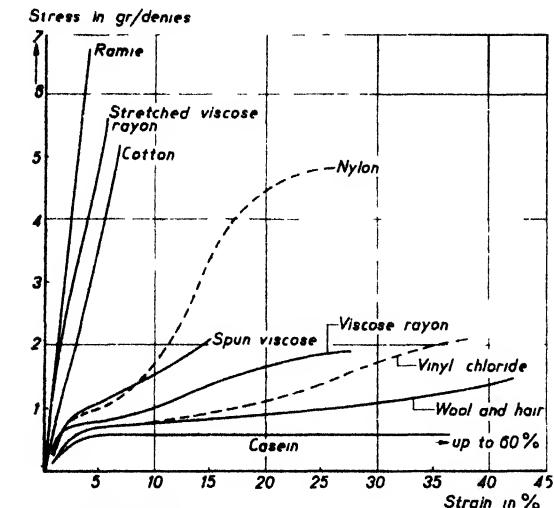
a. Stress-strain curves[1] (65% RH, 20° C, rate of loading 10 g/den/min).
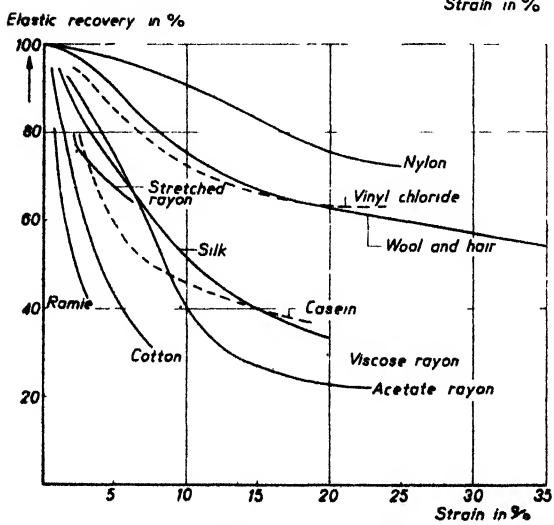
b. Elastic recovery as a function of the strain (duration of loading 0.5 min; duration of recovery 1 min).

Fig. 175. Comparison of the mechanical properties of some fibres [2].

[1] In order to calculate the stress in kg/cm², multiply the number of g/denier by 900 d, where d = specific gravity.

[2] R. MEREDITH, *Shirley Inst. Memoirs*, 19, July 1944.

Another kind of polyamides are the *poly-urethans*. These are formed by the action of isocyanates (—N = C = O) with, for example, OH-containing bodies. The H-atom of the OH group migrates to the N atom and an addition follows in which no by-products are liberated. Using di-isocyanates and alcohols with two or more functional groups, macromolecules of various types can be formed (Fig. 174).

These materials were developed in Germany on a commercial scale during the war [1]. At present some 15 different types are of commercial interest. One of the most important is the reaction product between 1,6-hexane di-isocyanate and 1,4-butyleneglycol [2].

The polyamide fibres have first-rate mechanical properties. Fig. 175a shows the stress-strain curve in comparison with other textiles; a strength of 5 gr/den. and an extensibility of 25% is a very favourable combination. On p. 208 it was already remarked, however, that especially for textile fibres the capacity of elastic recovery is still more important than the ultimate strength and extension at rupture. For this reason, the recovery is shown in Fig. 175b and here the outstanding position of Nylon is immediately obvious. It also clearly appears that rayon and casein wool are poor in this respect compared with natural fibres like wool and hair, although it must be said that they are better than materials like cotton and ramie.

The good mechanical properties of Nylon also show themselves in practical wearing tests, as appears from Fig. 176. Stockings were made with toes of
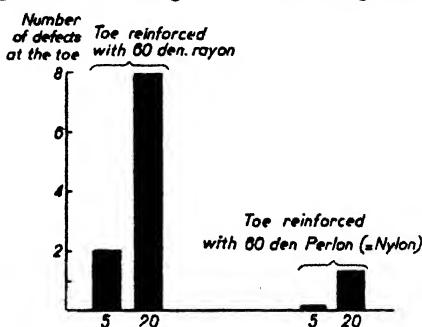
Fig. 176. Wearing experiments with stockings [3] (the figures 5 and 20 indicate the time of wear in days).

Nylon instead of rayon resulting in a reduction of the average number of defects to one third. These good mechanical properties only come into being below a certain moisture content; on drying, the fibres become brittle.

There are also other properties in which Nylon excels. Table 53 shows that the specific gravity of 1.14 is 10 to 30% lower than that of most other

[1] O. Bayer, *Modern Plastics*, 24 (1947) 149.
[2] Fibres made out of this product are called Perlon U, plastics are called Igamid U.
[3] J. Kleine, *Die Chemie*, 55 (1942) 179.

TABLE 53.

PROPERTIES OF SOME FIBRES [1]

	Fibre	S. G.	Moisture regain in % at 65 % R.H. [2]	Tensile strength in kg-mm²		Elongation at break in %		Loses strength above	
				dry	wet in % of dry	dry	wet	°C	°F
Natural	Wool	1.31	16	16	86	50	45	—	—
	Cotton	1.53	8	75	120	5	—	149	300
	Silk	1.25	10	43	85	22	—	—	—
	Glass	2.54	0	110	97	3	3	310	600
Synthetic	Rayon viscose	1.53	14	38	62	18	27	149	300
	Vinyl chloride	1.35	0	27	100	16	16	79	175
	Vinylidene chloride	1.72	0	74	100	25	25	77	170
	Casein	1.29	—	9	43	50	100	100	212
	Nylon	1.14	4	66	87	14	21	215	435

fibres. The moisture absorption is also very low, but it is often doubtful whether this is an advantage or not, because, for example for underwear and socks, the absorption of moisture is just what is required. The strength in the wet condition is 87% of that in the dry state, a figure comparable with that for wool and silk, and definitely better than for rayon. Casein is especially poor in this respect, vinylidene chloride especially good. Some advantages of minor importance are the great resistance to heat (see last column of Table 53), the excellent resistance to light, and the suitability for being dyed
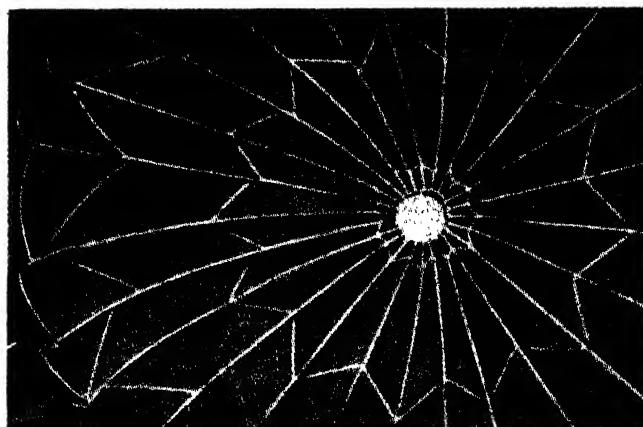
Fig. 177. Parachute made of nylon.

[1] W. D. Appel, Am. Dyestuffs Reptr., 34 (1945) 21.
[2] The moisture regain measures the absorption from zero to 65% relative humidity.

with those dyes generally used for wool and silk. The complete harmlessness in physiological respects and the resistance against the attack of enzymes, bacteria, mildew, and moths is also remarkable.

Nylon is not only applied for making clothes but also for parachutes and similar technical purposes. It is used for cords in airplane tyres; for automobile tyres it seems to be too extensible.

The application is not limited solely to textile purposes; the polyamides can also be used for dipping, calendering, moulding, extruding and injection moulding (see Table 54). We are concerned here with typical thermoplastics, which excel in a specially high impact strength. The electrical properties, especially in the wet state, are not very good, as may be expected when one considers the great many dipoles present.

TABLE 54.

PHYSICAL PROPERTIES [1] OF MOULDED POLYAMIDES (NYLON)

		J. M. 6339	J. M. 6337	J. M. 6377	F M 1
Tensile strength	kg/cm^2	280	530	670	740
	p s i	4,050	7,600	9,480	10,530
Impact Izod	ft. lb/in	14,200	152,000	70,500	290,000
Flow temperature [2]	°C	153	> 250	154	> 250
	°F	307	> 490	309	> 490
Power factor at 10^6 cycles		0.21	0.031	0.046	0.04
Water absorption in %		12.4	0.44	2.3	1.5

For the compression moulding process the material is used in powder form at 100 to 140° C (212—285° F). The injection moulding process requires a temperature of 150 to 200° C (302—390° F), depending on the type of material. As a consequence of its sharp melting point the forming process shows rather the character of a casting procedure; special machines have been developed for this purpose, working up to 270° C (530° F).[3] Up to now, the application for textile purposes is far more important than that for moulding.

The *poly-urethans* (Fig. 174), called Igamid U in Germany, are more resistant to solvents, acids, and water than the superpolyamides (2% water absorption against 8% for nylon). They have been used by the Germans for parachute fabrics, bristles, adhesives, and foam (s.g. 0.02).

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[1] Data from E.I. DuPont de Nemours & Co., Inc.
[2] The heat distortion temperature is much lower; it is of the order of 60° C (140° F).
[3] *Plastics Catalog*, New York 1945, p. 182.

POLYMERS BASED ON NATURAL RUBBER

Natural rubber or polyisoprene with the formula given in Figure 178,

$$\cdots \left[\begin{array}{cccc} H_2 & H & CH_3 & H_2 \\ | & | & | & | \\ -C-C=C-C- \end{array} \right]_n \begin{array}{cccc} H_2 & H & CH_3 & H_2 \\ | & | & | & | \\ -C-C=C-C- \end{array} \cdots$$
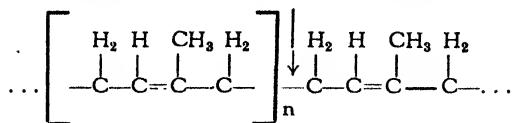
Fig. 178. Natural rubber.

contains long chain molecules with a molecular weight of about 500,000. The double bond gives the possibility of forming derivatives by *addition*, but *substitution* by exchange with the H-atoms can also occur. Oxidation takes place readily at the double bond. The C-C bond, indicated by ↓ is a weak spot at which the macromolecule can be broken by heating. Moreover, an *isomerisation* by cyclization can take place which leads to another group of derivatives.

Strictly speaking, *vulcanization* is the oldest method of making rubber derivatives. Since it is (contrary to our opinion) unusual to treat vulcanized rubber as a derivative, it will not be discussed in this book.

§ 65. CHLORINATED RUBBER

If chlorine could be added to the double bond, $C_5H_8Cl_2$ with 51% chlorine would be formed. In fact we find from 65 to 68% of bound chlorine, which shows that not only addition but also substitution takes place. The exact formula of chlorinated rubber is not known with certainty; presumably [1] it will be as shown in Figure 179.

$$\begin{array}{ccc} & CH_3 & \\ & | & \\ -CH-C-CH-CH_2- & or & \\ | & | & | \\ Cl & Cl & Cl \end{array} \qquad \begin{array}{cccc} & CH_3 & & \\ & | & & \\ -CH-C-CH-CH- & & \\ | & | & | & | \\ Cl & Cl & Cl & Cl \end{array}$$
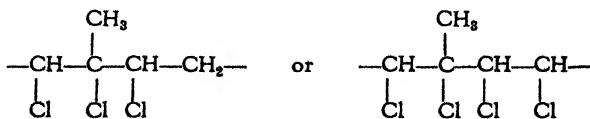
Fig. 179. Possible formulae of chlorinated rubber.

[1] A. NIELSEN, *Chlorkautschuk*,, Leipzig 1937. For a summary see H. BARRON, *Brit. Plastics,* **10** (1939) 420, 520.

It can however be taken for granted, that the product is cyclized to a considerable extent [1]. Chlorinated rubber is usually manufactured by passing chlorine gas through a rubber solution — generally in carbon tetrachloride. In order that the solutions may be sufficiently concentrated, the rubber is first depolymerized thoroughly on rolls in the presence of oxygen (compare page 230).

One of the most difficult problems in connection with the chlorination is how to avoid the formation of unstable products, which later on would lead to the splitting off of chlorine or hydrochloric acid.

The separation of chlorinated rubber from the solution is effected by distillation with water or by precipitation with non-solvents like alcohol or petrol. As the percentage of chlorine increases, the hardness, elasticity and chemical stability change. With 40% combined chlorine the material is still soft and extensible; with 54% it is hard. The higher the percentage of chlorine, the less easily are Cl_2 or HCl split off. A higher percentage than 68, corresponding to the formula $C_{10}H_{12}Cl_8$, cannot be attained. Good commercial products of this composition withstand a temperature of 100° C (212° F) without perceptibly losing chlorine (see below).

Chlorinated rubber is mainly utilized for the manufacturing of *lacquers*. This can be done either with or without oils, according to the purpose in view. Their application is restricted to purposes where a high quality is required because of their relatively high costs, e.g., for alkaline- and acid-proof concrete painting, anti-fouling and fireproof [2] coatings, printing ink, insulating varnish- and waterproof coatings. The best solvents are benzene hydrocarbons and esters.

Since the pure chlorinated rubber film, after evaporating the solvent, is brittle, it is usually plasticized. For this purpose, chlorinated diphenyls are specially suitable because, at the same time, they improve the adhesion. The lacquers can be pigmented in order to increase their stability to light. Very good lacquers result from combinations with phenol-formaldehyde resins, polyvinyls, and especially with alkyd resins.

In order to give an idea of the chemical resistance, we give [3] some data in Table 55.

An important point in which earlier products have often given unsatisfactory results is the aforementioned splitting off of chlorine. HOEKSTRA has found that at a temperature of 130° C (266° F) a maximum of 0.63%

[1] H. and HJ. STAUDINGER, *J. prakt. Chem.*, N.F. 162 (1943) 170.
[2] The fireproofing is due to a splitting off of HCl on heating.
[3] J. G. FOL and A. B. BIJL, *Bull. Rubber Growers' Assoc.*, 14 (1932) 210.

TABLE 55.

CHEMICAL RESISTANCE OF CHLORINATED RUBBER; LOSS OF WEIGHT
IN % AFTER 7 DAYS [1]

	Room temperature	Boiling water
H_2SO_4 (97%)	0.5	1.2
HCl (37%)	0.4	0.8
HNO_3 (65%)	0.4	0.5
KOH (50%)	0.5	1.0
$K_2Cr_2O_7$ and H_2SO_4	0.5	1.3

chlorine, and in a moist atmosphere about twice as much, is split off. Below 100° C (212° F) the speed of splitting off is practically zero. The conditions in a dry and in a moist atmosphere are shown in Fig. 180.
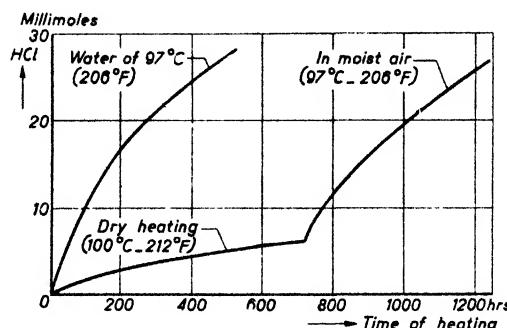
Fig. 180. Splitting off of hydrochloric acid from chlorinated rubber in a dry and in a moist atmosphere.

As mentioned already, the chlorinated rubber film is often rather brittle, especially if it is manufactured from types of rubber with a low viscosity (that means with a low molecular weight). On the other hand, from highly viscous solutions elastic films with a tensile strength of 400 to 500 kg/cm² (5,700—7,100 p s i) can be obtained, resembling those made from nitrocellulose.

In Fig. 181 is indicated [2] the influence of temperature on the strength and the elongation at rupture for a mixture of chlorinated rubber with softeners. Above 30° C (86° F) the sensitivity of the latter property suddenly becomes very great. This critical temperature can be influenced by the kind and quantity of plasticizer and filler. In this way it is possible to adapt the properties of the film, to a great extent, to the requirements.

Chlorinated rubber has very good electrical properties. In this connection

[1] J. HOEKSTRA, Kautschuk, 15 (1939) 108, 137.
[2] E. A. MOL, De Ingenieur, 7 (1940) MK 59.

it is important that the dielectric losses, as against those of certain cellulose derivatives (acetyl-cellulose), are scarcely influenced by the atmospheric humidity, as is shown in Fig. 182.
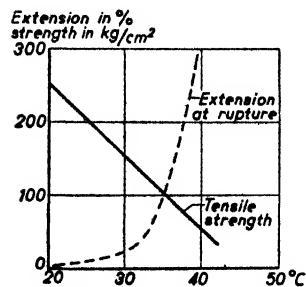
Fig. 181. In particular the elongation at rupture of a mixture of chlorinated rubber and softeners is strongly influenced by heating from 30° C (86° F) upwards.
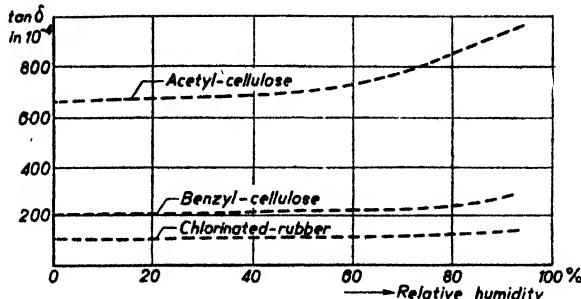
Fig. 182. The dielectric losses of chlorinated rubber are practically independent from the atmospheric conditions.

The influence of temperature on the dielectric losses and on the insulation resistance is not unimportant, but of the same order as that for cellulose derivatives. Hence, chlorinated rubber can often be used for insulation purposes, especially in combination with cellulose derivatives.

Attempts have been made to utilize chlorinated rubber as moulding material, but with little success. Some other applications are: films, filter cloth, artificial leather, adhesives.

§ 66. RUBBER HYDROCHLORIDE

In America, rubber hydrochloride is put on the market under the name of Pliofilm. The empirical formula is C_5H_8HCl, and as the chlorine adds itself most easily to the tertiary C atom, the greater part will have the following formula:

$$\ldots\text{—}CH_2\text{—}\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—}CH_2\text{—}CH_2\text{—}\ldots$$
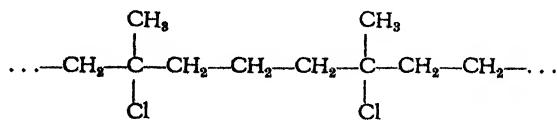
Fig. 183. Rubber hydrochloride.

It seems that the HCl-addition is also usually accompanied by a cyclization. Marketable products have between 28 and 35% of bound chlorine, which corresponds approximately to the theoretical maximum of 33.9%; they usually contain about 10 per cent of plasticizer, antioxidant, etc. They are stable up to 140° C (285° F).

The manufacturing process consists in passing hydrochloric acid gas through solutions of masticated rubber at a temperature of 5° C (41° F), and in certain cases under pressure. The films are prepared in film casting machines (see p. 202).

Fig. 184. Hand apparatus for the heat-sealing of Pliofilm.

On account of its being unaffected by acids (oxidizing acids excepted) and up to 20% KOH, and particularly because of its impermeability to water, rubber hydrochloride is used for impregnating, packing, etc. One of the most important applications is the packing of food because of its impermeability to moisture and its being absolutely odourless and tasteless.

TABLE 56.

WATER VAPOUR PERMEABILITY OF FILMS [1]

[25° C (77° F). Vapour pressure 20 mm. Rel. humidity 85%.]

	Permeability $P. 10^8$	Diffusion $D. 10^8$	Solubility h
Cellophane (regenerated cellulose)	4.7	0.39	1.2
Cellothene (0.4 mil coating)	0.25	0.36	0.07
Ethyl-cellulose	510	19.3	2.6
Koroseal (vinyl chloride)	5.6	0.39	1.8
Saran (vinylidene chloride)	0.007	0.13	0.06
Nylon I	3.7	0.20	1.8
Nylon II	260	1.1	24.
Pliofilm	1.3	0.15	0.88
Polyethylene	2.1	0.48	0.44
Glassine (waxed)	0.45	0.54	0.08

[1] P. M. Doty, W. H. Aiken, H. Mark, Ind. Eng. Chem., Anal. Ed., 16 (1944) 686.

Regarding the permeability to water vapour, the quality of Pliofilm is only surpassed by that of polyvinylidene chloride and by some materials with a special coating (Table 56). A comparison with the last-mentioned films, therefore, does not give good idea of the materials themselves.

The permeability P has been calculated from $P = Dh$ (formula 18, p. 65), where D is the diffusion constant and h the solubility. It appears that the better properties of vinylidene chloride are chiefly based on its very low solubility. The bad properties of cellophane are due to the high solubility of water and also to the high diffusion constant. For ethyl-cellulose the chief cause of the high permeability appears to be the quick diffusion, whereas, for Nylon II, it is the high solubility.

In consequence of the thermoplastic properties, Pliofilm can be heat-sealed at a temperature of 110° C (228° F.). In this way completely airtight seams can be obtained in a very simple manner. For this purpose a simple apparatus has been developed which can be operated by hand (Fig. 184). For mass-packing, automatic machines have been constructed. Fig. 185 shows how fruit can be wrapped in pliofilm in this way to prevent it from drying up.
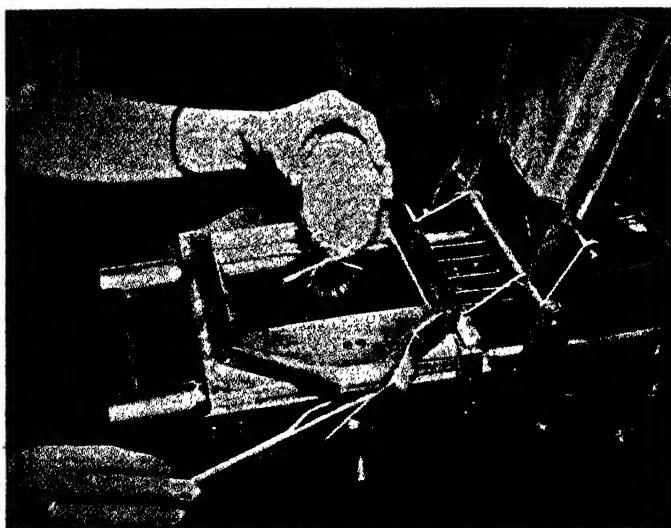
Fig. 185. Protection of fruit against drying up, using rubber hydrochloride foils.

Fig. 186 presents the stress-elongation curves of a few packing materials. What is particularly striking in the case of Pliofilm is the high elongation at rupture, amounting to about 400%; moreover, the resistance against tearing is very great. Consequently, Pliofilm is the most ductile and toughest organic packing material which is known so far. The properties are about the same

in the two principal directions, in contrast to cellophane, for example. This proves that during the manufacturing process only a very insignificant orientation has taken place.
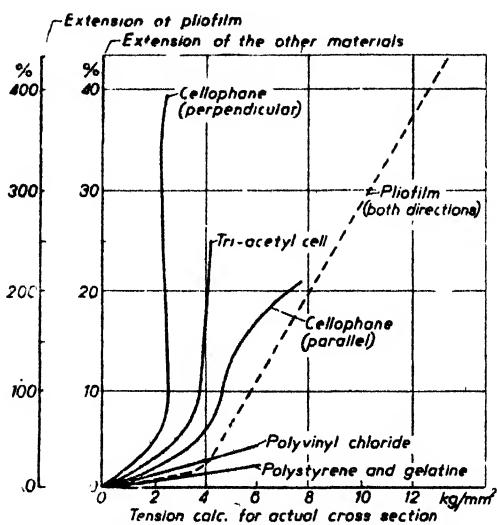
Fig. 186. Stress-elongation curves of some packing foils (note the different scales of the elongation axis).

It is possible, by extensive orientation, to manufacture fibres of considerable strength. One speaks of tensified Pliofilm, which reaches a strength of about 1500 kg/cm² (21,000 p s i), when recalculating the values for the actual area during the experiment, thus approaching that of well-vulcanized rubber. The elongation at rupture is about 30⁰/₀.

§ 67. OXIDATION PRODUCTS

The oxidation of rubber takes place preferably [1] at the double bond. In the example of Fig. 187 the formation of an aldehyde and of a ketone is
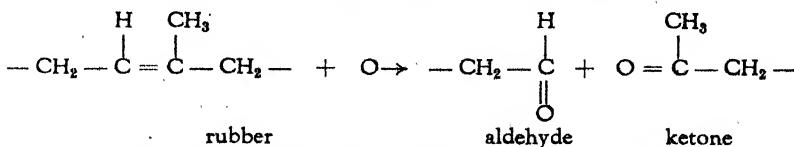
Fig. 187. Example of an oxidation reaction of rubber.

represented; however, further possibilites exist, e.g., the formation of alcohols or acids.

Consequently, one obtains a rather complicated mixture of chemical deriv-

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[1] See for other possibilities and their consequences: B. DOGADKIN, *J. Gen. Chem. USSR*, **15** (1945) 177.

atives which, moreover, can be of a different chain length. Such mixtures are known[1] in technology as "Rubbone".

To manufacture them, either a 50% solution of masticated rubber can be
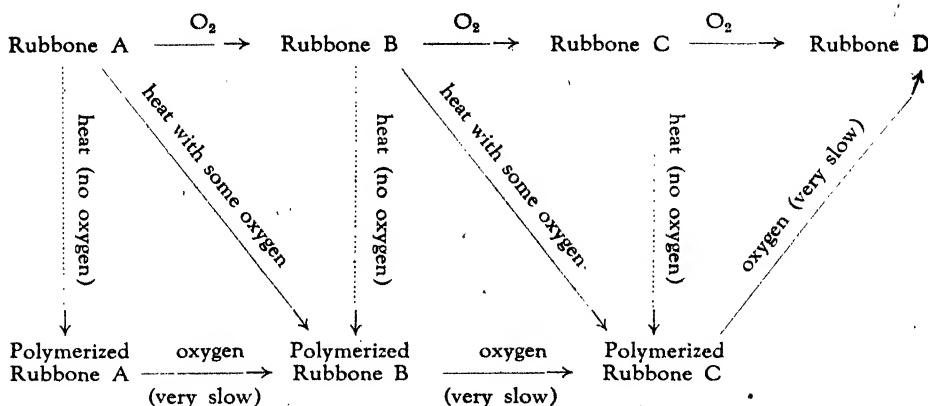
Fig. 188. Heat and oxygen polymerization of "Rubbone".

heated in an autoclave with 2.5% cobalt linoleate at the same time blowing through air, or the catalyst can be incorporated into the rubber on the rolls after which the compound is exposed to atmospheric oxygen.

A whole series of "Rubbones" are on the market. They can be regarded as resins which are capable of being heat- or oxygen-hardened. Fig. 188 shows the transitions occurring in this connection.

Rubbone B is the most important one, a yellow resin of the empirical formula $C_{10}H_{16}O$. It is a raw material for the lacquer industry, which can be mixed with nitrocellulose or bound to drying oils. The polymerization rate of Rubbone B is more or less adapted to that of the oils. Rubbone is also used for the manufacture of printing inks and glues. One of its most important properties is that when hardened it resists very high temperatures — for a short time up to 350° C (690° F). This has led to its utilization as a lacquer for electric insulations. Also of importance is its resistance to acids, alkalis, and organic solvents. A special application is given by its strong adhesion to asbestos; here mixtures with chlorinated rubber are used. The "Rubbones" can be vulcanized to some extent with sulphur.

§ 68. RUBBER ISOMERS

Many rubber isomers exist which differ from rubber and from each other only in their degree of saturation. The decrease of unsaturation is mostly

[1] H. P. STEVENS and F. J. POPHAM, Proc. Rubb. Tech. Conf., London, 1938, 337.

ascribed to a cyclization and therefore we sometimes also speak of cyclo-rubber [1].

Various substances are known which cause cyclization; the products thus obtained vary between gutta-percha-like compounds and brittle resins, and are called "Thermoprene". They are manufactured by kneading the raw
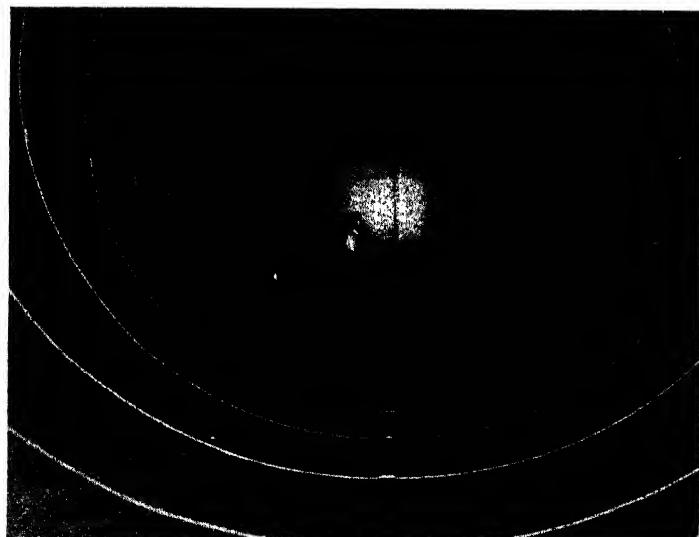
Fig. 189. Tank lined by Vulcalock process.

rubber with para-toluene-sulphonic acid, sulphuryl chloride, or chloro-sulphonic acid on rolls at a temperature of 130° C (266° F). Although certain thermoprenes lose 60 per cent of their unsaturation, all of them are capable of being vulcanized. They are used for fastening rubber to metal, stone, cement, wood, etc, (Vulcalock, Plioform, Vulcoferran). Fig. 189 gives an example. Cyclo-rubber is used in paper coatings for heat drying printing inks and as a compounding ingredient for natural and synthetic rubbers.

The lining of tanks has become very important. The adhesion to metal is so strong that the metal can be stretched far beyond the yield value without the thermoprene being loosened. At higher temperatures the method fails because thermoprene then becomes plastic; the maximum softening temperature which can be reached is about 130° C (266° F), the decomposition temperature 210° C (410° F).

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[1] H. BARRON, gives a summary: *Brit. Plastics*, 10 (1939) 585, 635, 632; 11 (1940) 86, 141.

§ 69. OTHER RUBBER DERIVATIVES

Besides those mentioned already, a great number of other rubber derivatives are known. We mention: brominated rubber, rubber hydrobromide, iodine rubber, rubber hydroiodide, fluorinated rubber, rubber hydrofluoride and rubber maleic acid [1] derivatives. None of them has so far become of much practical importance and therefore we shall not treat them further. The maleic acid derivatives have, of late, undergone a development in the direction of an improved swelling resistance [2].

[1] R. G. A. BACON and E. H. FARMER, *Proc. Rubb. Techn. Conf., London* 1938, p. 256.
[2] J. LE BRAS, *Rev. gén. caoutchouc,* 19 (1942), 43, 79.

CHAPTER XIV

SILICONES [1]

§ 70. CHEMISTRY

A new group of materials has recently entered the market under this name. They consist essentially of silicon-oxygen chain-molecules with organic side groups R, which are mostly CH_3.

By carrying out the GRIGNARD reaction[2] on silicon tetrachloride, three different series of organic silicon chlorides can be obtained which may be converted into the corresponding alcohols, these being polymerizable.

$$SiCl_4 + MgRCl \rightarrow MgCl_2 + RSiCl_3 \rightarrow RSi(OH)_3$$
silanetriol

$$\rightarrow -\overset{\underset{\displaystyle |}{R}}{\underset{\underset{\displaystyle O}{|}}{Si}} \cdot O \cdot \overset{\underset{\displaystyle |}{R}}{\underset{\underset{\displaystyle O}{|}}{Si}} \cdot O \cdot \overset{\underset{\displaystyle |}{R}}{\underset{\underset{\displaystyle O}{|}}{Si}} \cdot -$$
poly-sesquisiloxane

$$SiCl_4 + 2MgRCl \rightarrow 2MgCl_2 + R_2SiCl_2 \rightarrow R_2Si(OH)_2$$
silanediol

$$\rightarrow -\overset{\underset{\displaystyle |}{R}}{\underset{\underset{\displaystyle R}{|}}{Si}} \cdot O \cdot \overset{\underset{\displaystyle |}{R}}{\underset{\underset{\displaystyle R}{|}}{Si}} \cdot O -$$
Poly-siloxane

$$SiCl_4 + 3MgRCl \rightarrow 3MgCl_2 + R_3SiCl \rightarrow R_3Si(OH)$$
silaniol

$$\rightarrow R \cdot \overset{\underset{\displaystyle |}{R}}{\underset{\underset{\displaystyle R}{|}}{Si}} \cdot O \cdot \overset{\underset{\displaystyle |}{R}}{\underset{\underset{\displaystyle R}{|}}{Si}} \cdot R$$
Disiloxane.
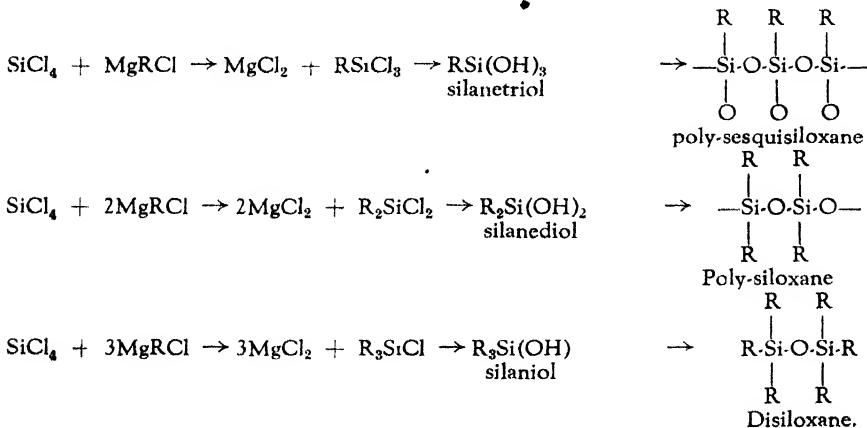
Fig. 190. Formation of silicones.

This GRIGNARD method has certain disadvantages. The very reactive solutions are difficult to handle, the inflammable solvents are dangerous, the by-product $MgCl_2$ has little value and the yield of the reaction is low. Some of these defects are avoided by the so-called "direct process", in which elementary silicon reacts directly with an organic chloride by means of a copper catalyst[3].

$$Si + 2 RCl \longrightarrow R_2SiCl_2$$
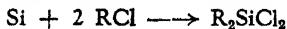
By varying the R-groups, a wide variety of materials is possible. It is clear

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[1] A summary is given by S. Z. BASS and T. A. KAUPPI, Trans. I.R.E., 33 (1945) 441; E. G. ROCHOW, Introduction to the Chemistry of Silicones, New York 1946.

[2] C. A. BURKHARD et al., Chem. Revs. 41 (1947) 97.

[3] E. G. ROCHOW, J. Am. Chem. Soc., 67 (1945) 963.

that the properties as high polymer products are due to the fact that the organic side-groups have only a weak secondary coherence compared with the strength of the Si-O bonds. This is the reason why the silicones do not have the character of a glass.

The types with linear molecules are soluble in organic solvents (toluene) and have a thermoplastic character. The polysesquisiloxane types are thermosetting and this can be controlled to such an extent that at only a few spots are bridges formed between the chain-molecules, thus leading to rubbery products.

The raw materials for producing silicones are sand (SiO_2), brine (to supply the chlorine to react with the silicon) and organic chlorides to make the magnesium compounds.

The silaniol more or less represents the monomer, although under the conditions of hydrolysis it usually condenses. The diols can form chain-molecules, thus yielding thermoplastics. In the literature it has not yet been reported which chain-lengths correspond to the various types, identified by a certain viscosity. The triols can build three-dimensional structures and thus they are of the setting type. They can form either hard resins or rubbers, depending on the degree of crosslinking.

TABLE 57.

PHYSICAL PROPERTIES OF FLUID SILICONES [1]

Type (after Dow-Corning)	Viscosity c. stokes at 25° C	Freezing point		Boiling point		S.G.	Use
		°C	°F	°C	°F		
D.C. 500	0.65	—68	—90	99	210	0.761	liquid dielectrics
	2.0	—84	—119	230	446	0.871	
	5.0	—70	—94	120-160	248-320	0.918	waterproof
	10	—67	—88	> 200	392	0.940	treatment
	50	—55	—67	> 250	482	0.955	lubricant
D.C. 200	100	—55	—67	—	—	0.968	
	500	—50	—58	—	—	0.972	
	1000	—50	—58	—	—	0.973	
D.C. 710	200	—22	— 8	—	—	1.095	lubricant at
	500	—22	10	—	—	1.112	high temp.
D.C. 701	9	—65	—85	320	608	1.023	thermal expansion fluid
D.C. 703	60	—36	—33	430	806	1.089	high vacuum oil

[1] Dow-Corning (Midland, Mich.) Silicone pamphlet 1945.

§ 71. APPLICATION AND PROPERTIES

a. *Liquid silicones.*

These are put on the market in a complete series, each member characterized by its viscosity. Table 57 shows some of the representatives, of which the chief characteristics are their stability against air and moisture, even at
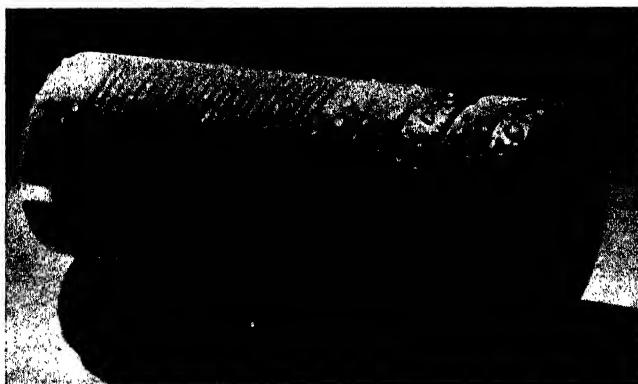
Fig. 191. Water repellency of silicone-treated ceramic surfaces.

their boiling point. The D.C. 500 series is recommended for application between —57° C (—70° F) and 94° C (200° F); the D.C. 200 series between —40° C (—40° F) and 210° C (400° F). The low volatility and vapour pressure
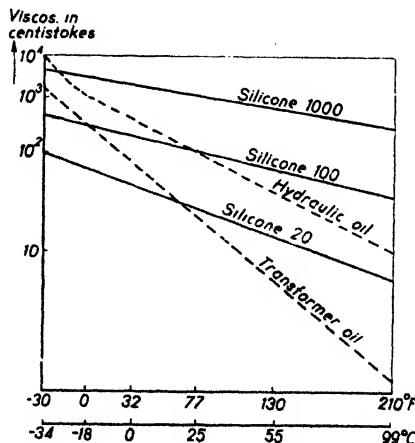
Fig. 192. Temperature-viscosity curves
for silicones and petroleum products.

make them suitable for use as high vacuum oil. The low power factor (6.10⁻⁴ at 10^8 cycles/sec.) and dielectric constant of about 2.4 make them applicable to electrical purposes. In this respect, the water repellency, when the silicones are applied as a varnish (see Fig. 191) is of special importance.

For the application as a lubricant, the low viscosity-temperature change is an interesting feature. Fig. 192 presents a comparison, in this respect, with petroleum oils. Comparing, for example, a silicone with a viscosity of 2000 centistokes (at—30° F) with transformer oil, the viscosity drops to 150 for the silicone and to 2 for the oil, by increasing the temperature from —35 to 100° C (—31 to 212° F).

TABLE 58.

PERCENTAGE OF WEIGHT LOSS AFTER 40 H AT 175° C (347ᶜ F)

High temperature petroleum grease A		58.3%
,, ,, C		34.8%
Silicone DC 31		5.2%
,, DC 44		3.3%

The thicker types of silicone are used as greases. Here also, the flat slope of the viscosity-temperature curve is important but the low percentage of volatilizable products may be mentioned, see Table 58. Moreover these greases do not harden or melt in a temperature range from 40 to 265° C (104—510° F).

b. *Solid silicones.*

The solid silicones can be applied in solution as varnishes; Fig. 191 showed their water repellant action. Thanks to their high temperature resistance even at long exposure (265° C = 510° F) they are specially suited as enamelling varnishes. This has led to the construction of electromotors of half the usual size. Other applications are the coating of glass fibres for magnet wire or for laminated materials.

Rubbery silicones (Silastic) are produced which are vulcanizable and have found application as "high-temperature rubbers", e.g., for gaskets. They are supposed to retain their elasticity for a long time at 200° C (392° F) and to withstand 300° C (592° F) for several days. They can be used continuously at 150° C (302° F) without deterioration. This resistance to oxidation is presumably connected with the lack of unsaturation.

The silicones are not yet produced on a large industrial scale; during the war about 20,000 lbs were manufactured altogether.

The tensile strength of 20 kg/cm² (330 lb./inch²) and the elongation at break of about 100% are indeed low figures for a rubber, but this is allowable for certain applications. In Table 26 further data about these silicone rubbers are to be found.

CHAPTER XV

MISCELLANEOUS POLYMERS

§ 72. POLYMERS DERIVED FROM NATURAL RESINS[1]

The efforts to improve natural resins have long ago led to the development of useful materials.

a. *Colophony.*

The neutralization of colophony by boiling it with $Ca(OH)_2$ or with ZnO until the acid number has decreased from 180 to about 60, serves to render the carboxylic group of the abietic acids (see Table 10, p. 18) harmless, thus removing the incompatibility of the colophony with basic pigments. At the same time a hardening of the resin is achieved and the product becomes usable for lacquers.

In order to make colophony more compatible with certain materials and to improve the weathering and the mechanical properties of the lacquer films, an esterification with glycerine is carried out. Esterified with methanol, cheap thick oils are formed which are used as plasticizers (Albalyn and Hercolyn).

With the aid of alkyd resins and oleic acids, products can be manufactured which have proved to be of importance for lacquer technology. However, because they possess only moderate weathering properties, the application is limited.

The double bonds of the abietic acid can be hydrogenated, leading to oxygen-proof resins (Staybelite).

With phenol-formaldehyde resins the so-called modified phenol resins are manufactured which are oil soluble and have found extensive applications; this has been already discussed on page 172. These products have greatly reduced the use of natural copals.

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[1] C. ELLIS, *The Chem. of Synthetic Resins*, New York 1935, p. 764—829.

b. *Copals.*

In this case also, an esterification with glycerine is carried out. Moreover, combinations with drying oils and with organic polybasic acids or with phenol resins are known. All these processes lead to improved raw materials for lacquers. By masticating on heated rolls (120—150° C = 248—302° F) the copal molecule can be decomposed to such an extent that the resin becomes soluble in alcohol.

c. *Shellac.*

During the last decade, especially, the organization of the united shellac producers has endeavoured to develop new derivatives of this resin. As an important ingredient of the shellac, aleuritic acid, a trihydroxypalmitic acid

$$HO - (CH_2)_6 - (CHOH)_2 - (CH_2)_7 - COOH$$
Aleuritic acid
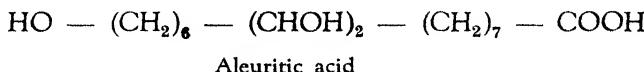
should be mentioned, the OH- and COOH-groups of which offer many possibilities for modification. On an average, five OH-groups are found in the shellac molecule. Altogether, more than ten different chemical compounds are found in shellac.

Shellac can be hardened by heating; hence, efforts have been made to increase the hardening rapidity to such an extent that competition with the phenol-formaldehyde resins might become possible. In fact, a certain acceleration can be achieved by adding 3% urea, but on this basis competition with Bakelite is still far from being possible.

The hydroxyl groups can be esterified, e.g., with fatty acids to produce waxy products.

The most extensive use of shellac is still in the unmodified state for gramophone records, in varnishes, for binder in felt hats and for the bonding of mica into arc-resistant insulators.

§ 73. POLYTERPENE AND COUMARONE RESINS

a. *Polyterpene hydrocarbon resins.*

These resins, the structure of which is represented below, are used as substitutes for alkyd resins in baking enamels. They are produced by the

catalytic polymerization of turpentine and range from viscous liquids to hard resins with a melting point of 150° C (302° F). They are thermoplastics and can be used for impregnating, coating, etc.

$$\left[\begin{array}{c} CH_3 \\ | \\ -C-CH_2 \\ | \\ \\ | \qquad | \\ \\ CH_3 \end{array}\right]_n \qquad \text{Polyterpene}$$
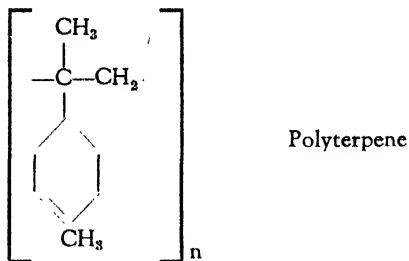
b.   *Coumarone - indene resins.*

The 150—200° C fraction of coal tar is rich in indene and coumarone. These are polymerized by sulphuric acid and after neutralization the resinous components are separated by distillation. A series of resins varying from a semi-fluid to a brittle state can be produced. Their hardness and colour are decisive for the applications. The resins are used in printing inks, in making flooring by mixing with asbestos, in lacquers and in blending with asphalts, rubbers, and oils (linoleum).

CHAPTER XVI

ECONOMIC ASPECTS

§ 74. GENERAL REMARKS

The development of synthetic polymers has been extensively stimulated by the war. For the synthetic rubbers this advance has been completely different from that of the plastics because practically all sources of natural rubber were cut off. We will therefore treat both groups separately in this chapter.

The idea is often expressed that we live in "a plastics age", or rather in "a plastics and elastics age". In our opinion we are still far removed from that state. This is clear from the following simple consideration: One can estimate the total world consumption of plastomers and elastomers at roughly 3 million tons per annum. The yearly consumption of cotton alone, however,
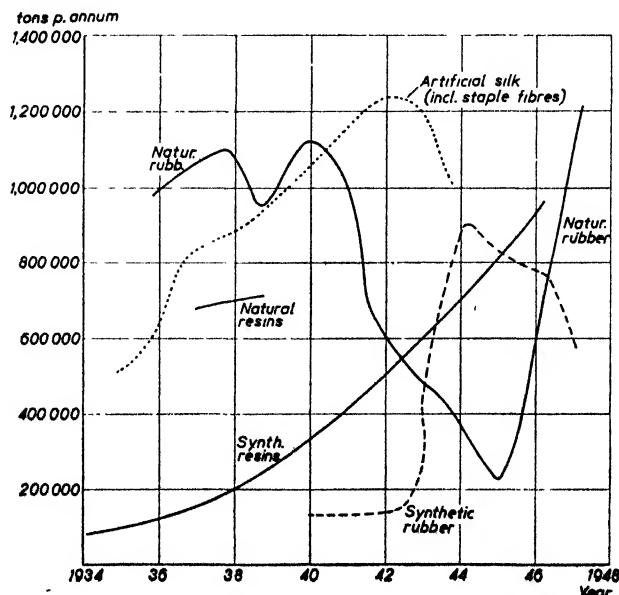
Fig. 193. World production of some high polymers.

amounted in 1945 to more than 5 million tons and that is only considering one of the many existing natural fibres, neglecting wool (1 million tons) and also other large groups of natural products like wood, metals, stone, etc. Pointing to the metals only, it appears immediately how relatively unimportant the plastics are. In 1940 the annual production of steel in U.S.A. was 60 million tons, that of plastics only about 0.4 million tons (half that of copper).

Notwithstanding this, the artificial high polymers play a much more important part than might be expected from their quantity. *They have found application in practically every branch* of industry and this makes them indispensable in our modern world.

Fig. 193 gives an idea of the world production of synthetic polymers compared with some natural materials. It appears that nowadays artificial silk, synthetic resins and natural rubber are of practically equal importance (expressed in the number of tons produced). For synthetic rubber the world production figures during the war have gone up at the same rate at which the production of natural rubber has fallen off, a point that will be discussed in § 76. Apart from the abnormal changes due to the war, a steady increase for all synthetic polymers can be observed.

§ 75. PLASTOMERS AND FIBRES

Doubtless, the *cellulose derivatives* still belong to the most important plastics, especially because rayon absorbs enormous quantities. Before the war, the total consumption was of the order of 1 million tons per annum; during the war this increased by 20%, but in 1944 there was a decrease again, to roughly 1 million tons owing to the stopping of the production in the defeated and invaded countries. Before and during the war the world production of the four main fibres was as follows[1]:

TABLE 59.

WORLD PRODUCTION OF FIBRES (IN 1000 TONS)

Year	Cotton	Wool	Nat. Silk	Rayon	Total
1939	6,000 = 73%	1,100 = 13%	55 = 1%	1,100 = 13%	8,000
1944	5,600 = 73%	1,100 = 14%	15 = 0.2%	1,000 = 13%	7,600

Figures concerning the production of artificial silk in various countries are given in Table 60.

[1] J. V. SHERMAN, *The New Fibres*, New York 1947.

The growth of the production of staple fibres for use in rayon filaments is remarkable. In 1935 they formed 20% of the total production of artificial silk; in 1940 and in 1944 this percentage was 52. It may be expected, however, that this proportion will decline again as soon as cotton is again abundantly available because, especially in the cotton-poor countries, staple fibre was used as an additon to cotton in the spinning of threads (Germany 1942: relation staple fibre to spun rayon = 80%, Italy 71%).

TABLE 60.

WORLD PRODUCTION[1] OF RAYON AND STAPLE FIBRE IN VARIOUS COUNTRIES (IN 1000 TONS)

	1938		1940		1944		1945	
	rayon	staple fibre	rayon	staple fibre	rayon	staple fibre	rayon	staple fibre
U.S.A.	115	13	175	36	250	75	180	75
Japan	95	170	101	135	13	37		
Germany	63	150	112	260	67	225		
Great Britain	48	15	45	23	36	27		
Italy.	46	74	45	105	23	67		
France	28	5	—	—	13	13		
Rest of the world .	50	6	52	25	68	76		
World total . . . . (approximately)	445	433	530	584	470	520		

In 1940 the ratio viscose: cuprammonium: nitro: acetate rayon was 79: 4: 1: 17. Especially in the U.S.A. acetate rayon was developed rapidly during the war; in 1945 it amounted to 28% of the total rayon filaments production as against 18% in 1934.

In 1945 the following average prices existed in U.S.A.:

TABLE 61.

PRICES FOR TEXTILES IN U.S.A.[1] (1945)

Viscose	{	staple fibre	25 ¢ per lb.
		rayon (150 den. Viscose)	55 ,,
		spun rayon from staple fibre 24/1	71 ,,
Natural fibres	{	cotton fibres	23 ,,
		cotton combed 36/1	67 ,,
		wool (raw)	118 ,,

The cellulose plastomers for moulding purposes include only a small

[1] *Rayon Organon*, Dec. 1945.

proportion of the cellulose derivatives. In 1939 they represented no more
than 5% of the rayon and staple fibre production, in 1944 about 3%. In
the U.S.A., their production [1] for 1947 was 42,000 tons against 16,000 tons
in 1939. These 42,000 tons were made up as follows:

TABLE 62.

PRODUCTION OF CELLULOSE PLASTOMERS (U.S.A. 1947, EXCL. FIBRES)

Cellulose acetate	35,000 tons
Cellulose nitrate	5,000 ,,
Various derivatives	2,000 ,,
(methyl, ethyl, benzyl)	
	42,000 tons

Of the acetate, 23% was used for sheets, rods and tubes, 77% as moulding
powder (injection moulding).

For the *synthetic resins* the figures of Table 63 are available.

TABLE 63.

ANNUAL PRODUCTION OF SYNTHETIC RESINS (IN TONS)

	1934	1935	1936	1937	1939	1946
U.S.A.	27,000	—	—	83,000	106,000	450,000
Great Britain	15,000	19,000	—	33,000		
Germany	16,000	25,000	32,000	45,000	154,000	
Rest of the World	4,000	—	—	4,000		
Total	62,000	—	—	165,000	260,000	

Fig. 194 gives an idea of the subdivison. The total sales for 1946 were about
450,000 tons, [2] which means 335 million dollars, or a unit value of $ 0.36 per lb.

Table 64 shows in more detail the increase of the main types of plastomers
in the U.S.A. after the war. Especially spectacular is the rise of ureas, mela-
mines, and polystyrene.

[1] *Modern Plastics*, **25** (1948) 70.
[2] *Modern Plastics*, **24** (1936) 124.

TABLE 64.

INCREASE OF PRODUCTION OF SOME PLASTOMERS AFTER THE WAR
(U.S.A.) (IN TONS) [1]

	1939	1946	1947
Phenolic (resins only)	25,000	75,000	100,000
Phenolic moulding powders (incl. fillers, etc.)	35,000	70,000	90,000
Urea and melamine resins	9,000	40,000	43,000
Urea and melamine moulding powders	—	—	15,000
Vinyl resins (excl. styrene)	500	70,000	80,000
Polystyrene	350	30,000	40,000
Cellulose derivatives (excl. rayon, etc.)	—	60,000	45,000
Alkyd resins	40,000	190,000	—

In Table 65, has been specified for what purposes the synthetic resins (phenolic, rosin ester, alkyd, urea, melamine, vinyl, styrene resins) are used. Protective purposes are most important, then follows moulding and casting. Some U.S.A. prices for moulding compounds are specified in Table 66; only the prices for overall types in large quantities are considered here.[2]

There is a general tendency to extend injection moulding and extrusion still more than compression moulding processes. This tendency is demonstrated by the number of machines in U.S.A., which increased between 1941 and 1947 as follows:
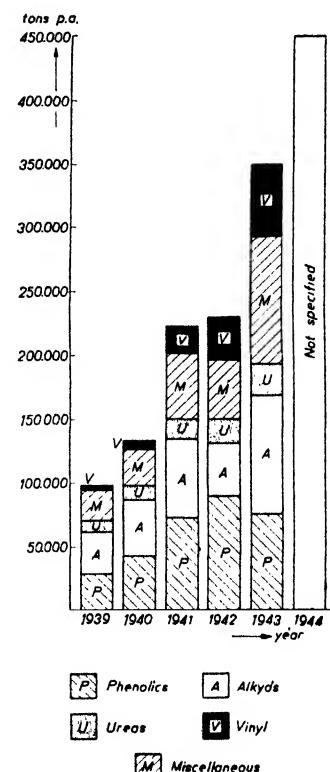
Fig. 194. Increase of the production of synthetic resins during the war [3].

P Phenolics   A Alkyds
U Ureas   V Vinyl
M Miscellaneous

[1] Modern Plastics, 25 (1948) 65.
[2] See for prices and produced quantities of resins in Germany: Modern Plastics, 23 (1945) 125 A, 157; Plastics Catalog, New York 1945, p. 43—50.
[3] Quantities and values based on net resin content only. Mod. Plastics, 25 (1948) 79.

Injection   from 1,000 to 3,600 machines
Extrusion   ,,   850 (in 1945) to 1,300   machines
Compression   ,,   8,000   to 13,000   ,,

TABLE 65.

THE USES OF SYNTHETIC RESINS (U.S.A. 1946)

Purpose	Production		Sales Value	Unit Value
	in tons	in %	in $ 1000	in ℮ per lb
Protective coatings	170,000	38	84,000	25
Moulding and casting	110,000	25	89,000	37
Laminating	16,000	4	10,000	29
Adhesives	35,000	8	18,000	23
Textile, paper and leather treatment	21,000	5	15,000	35
Miscellaneous	93,000	21	119,000	37
Total	445,000		335,000	

TABLE 66.

PRICES FOR MOULDING COMPOUNDS IN U.S.A. (1944/1945)

	℮ per lb
Phenol-formaldehyde	12 — 24
Urea-formaldehyde [1]	40
Melamine-formaldehyde [1]	45
Cellulose acetate	37
Cellulose acetate-butyrate	38 — 50
Vinyl	45
Acrylic	85
Polyethylene	75
Polystyrene	25
Nylon	60

In our opinion this tendency will become still stronger in the near future. There will, namely, be an overproduction of polystyrene, which will be the greater the more natural rubber will be available and the production of GRS will consequently be cut down (GRS consists of 30% styrene, see p. 128). Then polystyrene may be expected to be sold at a volume price of the same order of magnitude as phenolic moulding powders.

§ 76. ELASTOMERS

It has already been pointed out that for elastomers the situation was much more forced by the war than for plastics. The capitulation of Singapore

[1] In Germany, moulding powders based on urea were produced for 1 mark per kg, those on a melamine basis for 1.43 mark, making a much larger difference between the two types; G. M. KLINE, Brit. Plastics, 18 (1946) 174. This is presumably due to the fact that the Germans added more urea to the melamine.

suddenly cut off the Allies from their supplies of natural rubber and so an emergency programme for the production of synthetic rubber had to be carried out. Before the war, Germany produced roughly 100,000 tons of synthetic rubber per annum. The U.S.A., in record time, succeeded in building and operating the numerous huge plants necessary for its war demand of over one million tons p.a. Table 67 illustrates the situation.

TABLE 67.

PRODUCTION AND PRICES OF ELASTOMERS [1] (1947)

Type	Constitution	Production in tons	Price in ¢ per lb
G R S	Butadiene- styrene	430.000	18.5
G R I	Isobutylene-diolefin	55.000	18.5
G R M	Chloroprene	30.000	27.5
G R A	Butadiene-acrylic nitrile and numbered Bunas	7.000	—
	Polyvinyl chloride (plasticized)	70.000	—
	Total	592.000	—
	Natural rubber	1,200.000	21
	Grand total	1,792.000	—

From official reports [2] estimations of the out-of-pocket prices are known. These are especially interesting as regards GRS, because as soon as sufficient natural rubber will be available, a heavy competition between these two materials is to be expected. This out-of-pocket price is about 11 ¢ per lb. Adding a reasonable amount for selling costs, etc., it therefore may be expected that GRS can be sold at a price of say 15 ¢ per lb. Since natural rubber is superior to GRS for most purposes (tyres, see p. 140), it sells at a premium above GRS. From the fact, that before the war natural rubber could [3] be sold in U.S.A. for a price between 5 and 18 ¢ per lb, depending on the estate and on the type of producer, it appears that on this basis no great danger exists for natural rubber. Obviously, certain groups of the growers will not be able to compete on this basis, but this holds only for the minor part.

If not for military and political expedients, it would be impossible for important GRS plants to be kept running.

For the other rubbers indicated in Table 67, the situation is quite different, the special properties being important here. Each type finds its own applications regardless of the price of natural rubber, because the latter

[1] Rubber Statistical Bulletin, London Jan. 1948. The figures are estimated.
[2] Progress Report, War Production Board 12428 and 10171, Washington 1944.
[3] 'This was not done on commercial grounds.

cannot meet the special requirements (oil resistance, gas tightness, etc., see page 136).

Taking natural and synthetic rubber together, there will be an annual world production capacity of 3 million tons of rubber in the future. Estimating the future consumption at 1.5 million tons, half of the production will have to be cut. This will especially hit the GRS plants; the intention is to reduce the GRS production in the future to 200,000 tons p.a., that of special rubbers to 25,000 tons p.a. These quantities are considered necessary for military reasons. Another 600,000 tons capacity of GRS and 75,000 tons of special rubbers will be kept in stand-by condition for the same reason.

AUTHOR INDEX

SUBJECT INDEX