ORGANIC PLASTICS

By GORDON M. KLINE

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ABSTRACT

The increasing use of organic plastic materials by the various Government departments, coupled with a growing volume of requests for information concerning these products from the general public, made it desirable that a survey be made of their sources, properties, and uses. In addition to supplying this technical information on the broad aspects of this subject to Government officials and the public, detailed studies of some of these organic plastics have been made at the National Bureau of Standards in connection with research projects on leather substitutes, hat stiffeners, airplane dopes, and related problems.

This circular presents a summary of information assembled regarding those organic plastic materials which are of chief industrial significance, including the raw materials required, the chemical reactions involved, the various methods of processing, and the more important applications. The organic plastics are divided into four principal groups for discussion, namely, the synthetic resins, the natural resins, the cellulose derivatives, and the protein substances. The synthethic resins are subdivided into several chemical types as follows: Phenolic-aldehydic, amino-aldehydic, vinyl, hydroxy-carboxylic, indene, organic-polysulphides, and miscellaneous. Natural resins of animal, vegetable, and mineral sources are described. The chemistry of the cellulose esters and ethers and cellulose xanthate is outlined. The protein plastics considered include those prepared from casein, blood albumin, and soybeans.

Selected references are listed at the conclusion of the circular for the convenience of the reader who may be interested in further details regarding the manufacture, properties, and uses of organic plastics.

CONTENTS

CONTENTS—Continued

I. INTRODUCTION

What are "plastics"?   A dictionary definition of plastics as materials which are "readily responsive to shaping influences" does not place a convenient limitation upon this field.   It implies, but does not state, that the material should maintain its new form when the shaping influences are removed.   Even this more limited definition of a plastic would include a great variety of materials from the metals which are readily shaped when heated, to the solid rocks of the earth which exhibit zones of flow at great depths because of the pressure of the overlying mass.   The word plastic generally brings to mind a state of mushiness characteristic of bread dough or of the consistency of some asphalt pavings under a hot sun.   Certainly this condition is not easily associated with the firmness of a Bakelite one-piece telephone, the hardness of a Celluloid vanity set, or the rigidity of Beetleware tumblers.   These and other trade names for molded products are well known to the public.   Why should such materials be called plastics?   The statement that the resins and cellulose products from which these molded parts were made, have the property of softening when heated sufficiently, only serves to raise other questions.   Is a resin a rosin?   What is the difference between cellulose and Celluloid?   Where does Cellophane fit into this picture?   Will these molded products become plastic again if they are warmed?   Letters directed to this Bureau from all parts of the country indicate that these and similar questions regarding such materials are puzzling the average individual.   This circular has been prepared to answer such queries regarding the nature of molded products which are known only by nondescriptive trade names, and to show the relationship which exists between the various plastic materials.   Because the chemical nature of the raw materials from which plastics are made largely determines the properties of the finished products, primary emphasis has been placed upon presenting an introduction to the chemistry of plastics for the student, engineer, or executive who has had some chemical training but has not specialized in this field.   It is believed, however, that sufficient general information has been included to enable any interested individual to obtain a broad view of the nature of molded plastics, which are marketed under a confusing variety of trade names.

II. SCOPE OF THE MODERN PLASTICS INDUSTRY

The modern plastics industry deals chiefly with moldable materials manufactured from organic compounds, that is, combinations of carbon with hydrogen, oxygen, nitrogen, and other elements. The inorganic molding materials, such as concretes, cements, and ceramics, and also rubber, an organic substance, are not generally included within the scope of the plastic trade as it is known today, inasmuch as the industries utilizing these materials are considerably older and were already individually organized and developed prior to the advent of the newer plastics.

III. CLASSIFICATION OF ORGANIC PLASTICS ACCORDING TO CHEMICAL SOURCE

The four principal types of organic plastics are (1) synthetic resins, (2) natural resins, (3) cellulose derivatives, and (4) protein substances. A brief description of each of these groups will serve to indicate to the reader who is unacquainted with this field the essential characteristics of each type, and the distribution of the various commercial plastics according to this classification. Details concerning the preparation and properties of various members of each group will be found in later sections of this circular.

Public interest has probably centered largely upon the synthetic resin plastics because of their multiplicity and versatility. The chemist has been able to produce at will resinous materials having the hardness of stone, the transparency of glass, the flexibility of rubber, or the insulating ability of mica. These synthetic resins, in combination with suitable fillers, are readily molded into products characterized by excellent strength, light weight, dimensional stability, and resistance to moisture, moderate heat, sunlight, and other deteriorating factors. They lend themselves especially to the rapid manufacture of large quantities of accurately sized parts by the application of heat and pressure to the material placed in suitable molds and to the use of original or imitative effects in a variety of colors. Some of the cheap raw materials used in their production include phenol, urea, formaldehyde, glycerol, phthalic anhydride, acetylene, and petroleum. Synthetic resin plastics are known commercially under such trade names as Bakelite, Catalin, Beetle, Glyptal, and Vinylite. They are used in an ever-growing variety of applications, such as electrical parts, automotive parts, closures, containers, costume accessories including buttons, buckles, and jewelry, hardware, table and kitchen ware, and various novelties. The powdered molding compositions are generally sold to custom molders, who produce the finished products. The casting resins and laminated resinous products, described in more detail later, are, however, usually made into sheets, rods, or tubes by the manufacturer of the resin. Blanks are cut from these for the preparation of the finished product by machining operations.

The natural resins are more familiarly known to the public by their common names, such as shellac, rosin, asphalt, and pitch, than by the proprietary names attached by manufacturers to molding compositions prepared from them. They are used in industry for the production of the fusible type of molded product as distinguished from the

infusible articles formed by some of the synthetic resins. The asphalts and pitches are mixed with fillers such as asbestos in the preparation of so-called "cold-molded" plastics. The material is subjected to pressure in the mold and is immediately ejected without waiting for "curing" in the mold. The molded parts are transferred to ovens where many hundreds of pieces are cured at one time. These cold-molding compositions are used in the manufacture of electrical parts, handles, knobs, dials, and the like. They are not as strong mechanically as the synthetic resin plastics, nor can the molded pieces be made as thin or the dimensions held to such close tolerances as in the case of the synthetics. They are usually restricted in color to black or dark shades. They offer advantages, however, where heat resistance is a factor or in large dense pieces which would be quite expensive if a corresponding quantity of hot-molding material were required. Also, this type of product is particularly adapted to applications in which the total number of pieces is comparatively small, because the rapid molding process permits the use of a relatively inexpensive single-cavity mold. Cold-molding compositions are designated by various trade names, as Gummon, Cetec, and Thermoplax.

Hot-molding compositions are prepared from natural resins, for instance by mixing shellac, rosin, and asphalts with suitable fillers. The mixture is molded under pressure in heated molds, and after cooling, the shaped article is removed therefrom in final form. Trade names for such products are Compo-site and Lacanite. Compositions containing chiefly shellac as the binder are used in electrical insulators for high-voltage equipment, in telephone parts, and in phonograph records. Plastics prepared from natural resins are generally made into the molded product by the original manufacturer rather than marketed as the molding powder.

The third type of organic plastics, the cellulose derivatives, is probably the most widely used and best known of any of these materials. To this group belong Celluloid and other cellulose nitrate plastics used for making toys, toilet ware, pen and pencil barrels, and the like; cellulose acetate commonly used in the Celanese type of rayon and as a substitute for the slightly less expensive nitrated product when nonflammability is desired; and regenerated cellulose familiar to nearly everyone as the wrapping material Cellophane and the common or viscose type of rayon. The basic raw material, cellulose, is obtainable in fairly pure, fibrous condition as either ordinary cotton or pulped wood. Treatment with suitable chemicals converts cellulose into compounds which are characterized by the ease with which they can be formed into desired shapes. Cellulose plastics excel in toughness and are especially useful in thin sheets which have remarkable flexibility. These plastics conduct heat slowly and can be made substantially tasteless, odorless, and transparent. Their principal applications in addition to those mentioned above include photographic film, safety glass, flexible window material, artificial leather, airplane dopes, and lacquers.

The protein plastics are perhaps best known according to the source of the raw material, for example, casein from skimmed milk and soybean meal from soy beans. These protein substances are thoroughly kneaded into a colloidal mass, which is then formed into sheets, rods, or tubes by suitable presses or extrusion devices. The formed pieces

are hardened by treatment with formaldehyde. The finished prod-
ucts, such as buttons, buckles, beads, and game counters, are ma-
chined from blanks cut from the hardened material. The protein
plastics have the property of absorbing considerable moisture and,
therefore, have a marked tendency to warp. This makes them
unsuitable for large pieces or thin sheets. They can be readily pre-
pared in a variety of color and mottle effects. This material is
marketed in this country under such trade names as Ameroid and
Ronyx.

IV. CLASSIFICATION OF ORGANIC PLASTICS ACCORD-
ING TO EFFECT OF HEAT

The plastics used in the molding industry may be divided into two
groups based on their behavior toward heat, namely, (1) thermo-
plastic and (2) thermosetting. The thermoplastic materials are
permanently fusible, that is to say, they alternately melt or soften
when heated and harden when cooled. If they are subjected to very
high temperatures, vaporization or decomposition takes place. The
cellulose derivatives, some synthetic resins, and most of the natural
resins are examples of this type. The thermosetting plastics, on the
other hand, may be made permanently infusible. This group is
usually further subdivided into three stages on the basis of changes in
chemical and physical properties. The product of stage A is called
the initial condensation product and may be liquid or solid; it is both
fusible and soluble. The intermediate or stage B product is insoluble
and difficultly fusible, but it can be molded by the proper application
of heat and pressure. This is the usual condition of the resin in the
molding composition when it is received from the manufacturer.
Further heating of this material, as in the process of molding, con-
verts it to the final or stage C product, which has a permanent set
and maximum hardness, strength, resistivity, and insolubility.
Most of the molded products of synthetic-resin composition which
are now on the market belong to the thermosetting type.

V. FORMATION OF PLASTIC MATERIALS

1. PHYSICAL FORCES

The forces leading to plasticity are recognized to be both physical
and chemical. The physical causes will be briefly summarized. A
mixture of unlike molecules is generally involved. Just as in the
inorganic field many simple chemical compounds may unite to form
a complex but characteristic mineral ore, from which it is difficult to
separate the original constituents, so with organic substances a mix-
ture of two or more compounds is not marked by the well-defined
physical attributes of the pure compounds. Instead of separating
from solutions or solidifying in characteristic crystals, mixtures of
organic compounds tend to form amorphous or vitreous masses. Like-
wise, such mixtures do not display the sharpness of melting point which
marks a pure compound, but pass from the solid to the liquid state
over a considerable range of temperature. The molecules which make
up an organic plastic may differ by being isomeric, homologous, or
heterogeneous compounds. Isomers are compounds which are alike

in chemical composition, but which differ in the spatial arrangement or points of attachment of the atoms. Strictly speaking, homologs are compounds which are chemically related, but differ from member to member in composition by one atom of carbon and two atoms of hydrogen. In speaking of plastics, this term might be more broadly applied to include macromolecules built up of varying numbers of a simple monomeric unit, and also molecules of different degrees of esterification, such as cellulose mono-, di-, and triacetates. Heterogeneous compounds, such as paraffins, alcohols, acids, and esters, are present together in many of the natural waxes. The compounds which make up these various types of mixtures are usually soluble in one another and tend to form so-called solvate complexes, from which it is a difficult task to separate the original materials. The large size of the molecular units brings about chemical inertness which is quite characteristic of plastic masses. Finally, it should be noted that the colloidal nature of the aggregates contributes largely to their physical behavior, particularly with reference to their characteristic flow and formation of films.

2. CHEMICAL PROCESSES

The organic chemistry of these plastic masses has always been considered obscure and fortuitous, and it is only within recent years that a degree of order and regularity in their formation has been noted. The chemical processes which give rise to resins may be divided into two groups, (1) addition reactions and (2) condensation reactions. A type of resinifying mechanism consisting of the association of molecules may occur with some compounds saturated from the structural viewpoint. This is rather a physical process than a chemical combination, but its occurrence is linked with the presence of certain characteristic groups in the molecule. Thus, this behavior is especially prevalent with hydroxyl compounds, cyclic ethers, lactones, lactides, and acid anhydrides. It is analogous to the ordinary state of water, which is not simply H_2O, but an aggregate $(H_2O)_n$, composed of several unit molecules.

The formation of resins by strictly addition reactions is limited to compounds containing an unsaturated group capable of reacting within itself. Noteworthy among such resinogenic groups are the ethine $-C \equiv C-$, ethylene $>C=C<$ (nonbenzenoid), carbonyl $>C=O$, azomethine $>C=N-$, and nitrile $-C \equiv N$. The agencies which ordinarily effect the polymerization of compounds with these groups present are heat, light, and chemical catalysts.

Condensation reactions are characterized by the linking together of atoms with the accompanying elimination of elements, such as hydrogen or nitrogen, or of simple compounds, such as water, hydrochloric acid, hydrogen sulphide, or sodium bromide. Condensations may take place intramolecularly, as in the case of the formation of phthalic anhydride from phthalic acid, or intermolecularly; the latter may result from reaction between like molecules, such as the formation of diphenyl from benzene, or between unlike molecules, as, for example, the reaction between urea and formaldehyde. The agencies employed to carry out condensation reactions depend largely upon the material liberated. Some means of removal of this product is usually required, such as heat to vaporize it, an absorptive material to fix it,

or precipitation of one of the reaction products. In many instances catalysts are used to accelerate the formation of plastic masses by condensation reactions.

VI. SYNTHETIC RESIN PLASTICS

The first group of the organic plastics mentioned in the introduction, namely, the synthetic resins, may be subdivided into several chemical types as follows: (1) phenolic-aldehydic, (2) amino-aldehydic, (3) vinyl, (4) hydroxy-carboxylic, (5) indene, and (6) organic-polysulphides. There are, of course, many other classes of organic compounds which will react together to form resins, as a survey of the patent literature on this subject will indicate. The resins which are included in the above list, however, are those which are of chief industrial importance, and a summary of the raw materials and reactions entering into their preparation will, therefore, be of interest.

1. PHENOLIC-ALDEHYDIC RESINS

(a) PHENOL-FORMALDEHYDE RESIN

The phenolic-aldehydic type is from the standpoint of volume of production the leading industrial member of the synthetic resins. The raw materials are generally formaldehyde CH_2O, and phenol (also known as carbolic acid) or technical cresol consisting largely of metacresol with smaller amounts of the ortho- and para-isomers.
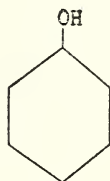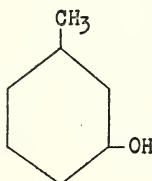
Phenol[1])   Metacresol

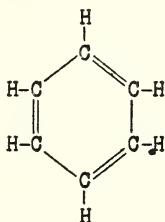[1] The figure ⬡ is an abbreviation of the Kekulé structural formula for benzene:

The replacement of the hydrogen atoms by other elements or radicals is indicated by placing the atomic symbols at the corners of the figure corresponding to the carbon atoms affected.
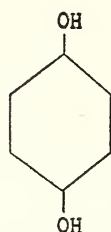
In addition to these, other compounds containing phenolic groups, such as pyrocatechol, resorcinol, or hydroquinone can be used and
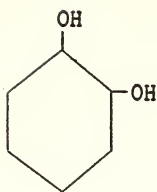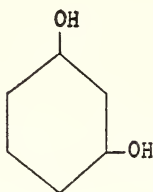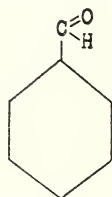
Pyrocatechol   Resorcinol   Hydroquinone

also various aldehydes, such as acetaldehyde or benzaldehyde, but it will be noted in the following paragraphs that the simpler members


Acetaldehyde   Benzaldehyde

of the various chemical groups are the ones commonly employed. These are usually cheaper, more readily available, and more reactive than the compounds of higher molecular weight. Phenol, like cresol, is obtained as a by-product of the coal distillation industry, or it is prepared synthetically by processes such as the alkaline hydrolysis of chlorobenzene. Formaldehyde, which is normally a gas, is made by the catalytic oxidation of methyl alcohol. It is usually obtained as an approximately 37-percent solution in water, under the name "formalin", or is converted to a solid for use in dry processes of resin formation by polymerizing the gaseous product to paraformaldehyde $(CH_2O)_3$, also known as paraform and trioxymethylene, or by treating it with ammonia to form hexamethylenetetramine $(CH_2)_6N_4$. On account of the expense of the anhydrous aldehyde materials, the wet process of manufacture is generally used.

The formation of a resin from phenol and formaldehyde may result in fusible or infusible products depending upon whether acid or alkaline catalysts are used. In the presence of acid catalysts one mole of formaldehyde may react with two moles of phenol:

$$2\ C_6H_5OH + CH_2O \xrightarrow{-\ H_2O} CH_2(OC_6H_5)_2 \xrightarrow{\text{rearranges}} CH_2(C_6H_5OH)_2$$
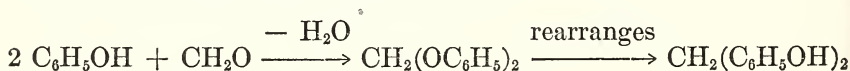
The product of further condensation in this case is permanently soluble and fusible. This type of resin is used in varnishes and lacquers. With alkaline catalysts the phenol and formaldehyde may combine in a 1:1 ratio, for which reaction Baekeland has proposed the following mechanism:

$$2\ C_6H_5OH + CH_2O \xrightarrow{-\ H_2O} CH_2(C_6H_4OH)(OC_6H_5) \xrightarrow{+\ CH_2O}$$
$$CH_2{=}C(C_6H_4OH)(OC_6H_5) + H_2O$$
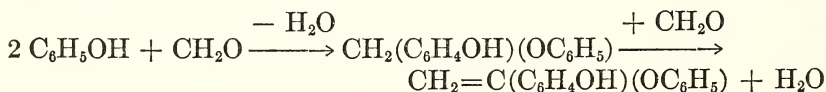
Further reaction resulting in hardening and loss of solubility and fusibility may take place by polymerization:

$$n \ (C_{14}H_{12}O_2) \longrightarrow (C_{14}H_{12}O_2)_n$$
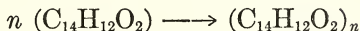
This type of phenol-formaldehyde resin is used in the molding industry.

(b) PHENOL-FURFURAL RESIN

Another commercial resin of this type is prepared by the reaction of phenol with furfural, an aldehyde which can be obtained from vari-

Furfural

ous natural sources, such as oat hulls, cornstalks, and the like by distillation with acid. Furfural, in addition to the active carbonyl group, consists of an oxide ring with two ethylenic linkages, all of which tend to make it a particularly reactive compound. The products of the phenol-furfural reaction may be either liquid or solid, depending upon the time of reaction and the percentage of furfural. Acid catalysts, in general, produce infusible products unless considerable excess phenol is present. Alkaline catalysts yield resins from p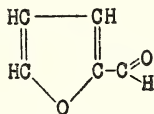henol and furfural which are better adapted to molding. It may be of interest to note that in addition to providing a plentiful supply of furfural for use in plastics, natural products such as cornstalks, cotton-seed-hull bran, and wood also contain compounds known as lignins, which include phenolic groups in their complex molecular structure. Considerable research has been carried on for the purpose of utilizing the potential reactivity of these natural lignins to produce an inexpensive resin with satisfactory molding properties. Although progress has been made experimentally, such products have not as yet appeared on the market.

(c) METHODS OF PROCESSING

(1) *Molding.*—The phenolic-aldehydic resins may be converted into useful products by the three general methods for the fabrication of plastic materials, namely, molding, casting, and laminating. For use in molding compositions the resins are incorporated with fillers which not only reduce the cost, but also by proper choice impart desirable qualities to the finished product. Wood flour, for example, when properly admixed, gives a product having suitable flow with less shrinkage and greater toughness. Where resistance to heat is required, finely divided asbestos is employed in place of wood flour. Low-friction products useful as dry bearings are prepared with a powdered graphite filler. The mixing operation is an important step in the process. Wood flour is sifted and dried; it is then mixed with the powdered, uncured resin and the two are ground together until thoroughly incorporated. The mixture is run between hot rolls and the cooled mass ground to a powder and sifted. The molding operation is carried out in hydraulic presses under pressures of one or more tons per square inch and temperatures ranging from about 150 to

175° C (302 to 347° F). Low pressure is used to close the press, permitting the material to distribute itself better and thereby placing less strain on the steel mold.

Products made with these resins possess those general properties which are characteristic of the organic plastics, namely, resistance to atmospheric and chemical corrosion, high structural strength, lightweight, low heat conductivity, and good electrical-insulation value. The molded products are usually made in black or brown colors; the light colors can be obtained, however, at an increased cost. The many uses of the phenol-formaldehyde molded parts include applications in the automotive, electrical, radio, telephone, building, and decorative fields as well as for novelties and packaging accessories. Some of the trade names of phenol-formaldehyde molding compositions are Bakelite, Durez, Haveg, Makalot, and Resinox. Durite is the name applied to a phenol-furfural product.

(2) *Casting.*—Phenolic resins for use in a casting process usually contain a larger percentage of formaldehyde than the molding resins and are not mixed with fillers. They are poured in a sirupy state into molds where they are hardened by slow baking. Inasmuch as a considerable period is required for the curing of such products, they are customarily cast as sheets, rods, or tubes, and the finished articles are machined from blanks. The cast resinous products lend themselves readily to a variety of beautiful color effects and a finish comparable to that of precious stones. They are widely used for clock cases, lamp shades and bases, jewelry, and related merchandise where their characteristic physical properties add charm and distinction to strength and durability. Cast phenolic resins are variously known on the market as Catalin, Marblette, and Fiberlon.

(3) *Laminating.*—The third method of making useful products from phenolic-aldehydic resins consists in employing them as binders for cloth or paper. These laminated materials are prepared by impregnating the sheets with a solution of the resin while it is still in the A stage, drying, and then bonding many layers together by the application of heat and pressure. This treatment converts the resin to the C stage and yields a hard, dense product which will not delaminate and which possesses excellent mechanical and dielectric properties. The choice of filler, whether cotton or asbestos cloth, rag or kraft paper, depends upon the use to which the finished article is to be put. Phenolic laminated materials find many applications in the automotive, railroad, aircraft, telephone, power, and building industries. A particularly important use is as silent gears in industrial machinery of many types from automobile timing equipment to high-pressure pumps. Some of the trade marks of these products are Formica, Micarta, and Textolite.

2. AMINO-ALDEHYDIC RESINS

Although research has disclosed that many resinous substances are obtainable by the interaction of aldehydes and amines, only two of these have become important commercially, namely the

urea-formaldehyde and thiourea-formaldehyde resins.　Urea has the structural formula:

$$
\begin{array}{c}
N<_H^H \\
| \\
C=O \\
| \\
N<_H^H
\end{array}
$$
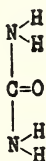
It is made industrially either from calcium cyanamide or from ammonia and carbon dioxide.　In thiourea, which is a by product of the gas industry, there is an atom of sulphur, instead of the oxygen atom in urea.　The reaction products of urea and formaldehyde are dependent upon the character of the condensing agent and the proportions in which the two ingredients are brought together.　The reaction in alkaline solution involves the preliminary formation of mono- or di-methylolurea:

$$NH_2CONH_2 + CH_2O \longrightarrow NH_2CONH(CH_2OH) \xrightarrow{+ CH_2O}$$
$$NH(CH_2OH)CONH(CH_2OH).$$

Treatment of these compounds with acids or with heat alone causes the loss of water and results in the formation of an azomethine radical, which is an active polymerizable group:

$$NH_2CONH(CH_2OH) \xrightarrow{- H_2O} NH_2CON=CH_2.$$
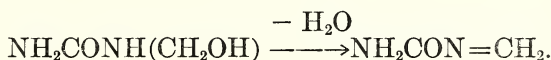
In acid solution methyleneurea is formed directly from urea and formaldehyde:

$$NH_2CONH_2 + CH_2O \longrightarrow NH_2CON=CH_2 + H_2O.$$
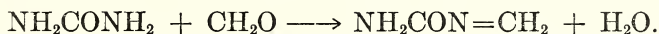
These unsaturated compounds are not isolated as such, but react with one another to form polymers of varying composition.　This process may be represented as:

$$x\ (C_2H_4ON_2) \longrightarrow (C_2H_4ON_2)\ _x,$$
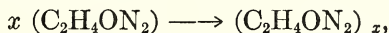
with the proviso that additional molecules of formaldehyde and water may be involved.

The reaction of thiourea and formaldehyde follows a similar course. In addition thiourea and its derivatives may split out hydrogen sulphide to form the resinogenic carbodiimide group, $-N=C=N-$, which undergoes polymerization.　Thus, diphenylthiourea may react as follows:

$$NH(C_6H_5)CSNH(C_6H_5) \xrightarrow{-H_2S} C_6H_5N=C=NC_6H_5 \xrightarrow{x\ moles}$$
$$(C_6H_5N=C=NC_6H_5)_x.$$
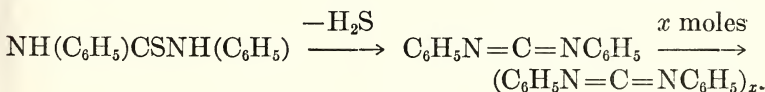
The urea-formaldehyde resins are colorless and are readily converted into transparent and translucent molded products of many colors. They are supplied to the molders in an intermediate stage of polymerization and curing in molds under heat and pressure is necessary to obtain the finished article.

Urea-formaldehyde molding compositions are used particularly for articles in which color and appearance are important, such as containers and bottle closures. The fact that they are tasteless, odorless, and water-resistant has made possible their successful use for tableware. Other important applications include buttons and buckles, premium items, and automobile fixtures. The molding compositions are known under such names as Beetle, Plaskon, and Unyte.

3. VINYL RESINS

(a) POLYESTERS OF VINYL ALCOHOL

The third type of the synthetic resins listed above is characterized by the presence of the unsaturated radical $CH_2=CH-$, called vinyl. The products of the polymerization of vinyl chloride and vinyl acetate, esters of vinyl alcohol $CH_2=CHOH$, are well-known members of this group. These esters are prepared by the action of the respective acids on acetylene:

$$CH \equiv CH + HCl. \longrightarrow CH_2=CHCl.$$
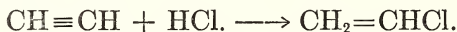
They polymerize readily under the influence of heat or light and catalysts to form thermoplastic resins. The usual conception of the structure of such resins is that they exist as chains of various lengths formed from the original monomer:

$$2\ CH_2=CHCl \longrightarrow -CH_2-CHCl-CH_2-CHCl- \xrightarrow{+CH_2=CHCl} -CH_2-CHCl-CH_2-CHCl-CH_2-CHCl-,\ \text{etc.}$$
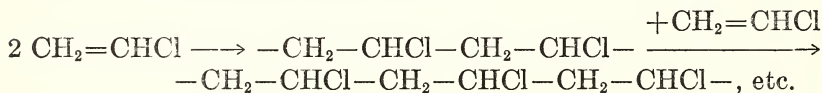
Plastic products composed of resins formed by the co-polymerization of vinyl chloride and vinyl acetate are known in this country as Vinylite. They are thermoplastic and have low softening points, approximately 70° C (158° F). They are odorless, tasteless, and resistant to moisture, dilute acids and alkalies. Their transparency, toughness, and relatively slight absorption of water have been important factors in their use as dentures. Such denture compositions, containing small amounts of pigment, are marketed under the names Resovin and Vydon. Another important use is in the manufacture of phonograph records. Because of their greater strength and flexibility, and their superior grooving characteristics, such records can be made about one-fifth as heavy as the ordinary shellac record. The vinyl resins have also found application as protective coatings for cement and as lining for cans. Vinyl resins formed entirely from vinyl acetate are also available under the names Mowilith and Gelva. Hydrolysis of such resins results in the freeing of alcohol groups within the molecule which are capable of reacting with aldehydes. Treatment of hydrolyzed vinyl acetate resin with formaldehyde forms a harder resin with a higher softening point and known as Formvar; acetaldehyde yields a related product called Alvar.

(b) POLYSTYRENE

Another resinous product of this type is made from styrene, $C_6H_5CH=CH_2$, sometimes called styrol. Because of the expense of producing this compound, these resins are made commercially without attempting to isolate the styrene, by the action of heat on ethylbenzene with or without the addition of chlorine. A chain structure similar to that shown above for vinyl chloride is generally attributed to styrene resin. The relatively high cost of producing these resins has prevented them from attaining the industrial position to which their excellent transparency, strength, and dielectric qualities would otherwise bring them. Styrene plastics are employed chiefly for insulating parts in high-frequency service, especially in radio applications where low electrical losses are important. The trade name Victron is used for a styrene resinous product made in this country.

(c) POLYESTERS OF ACRYLIC AND METHACRYLIC ACIDS

Among the more recent of the commercially available resins are the polymers of the esters of acrylic acid, $CH_2=CH-COOH$, and methacrylic acid, $CH_2=C(CH_3)-COOH$. The reactions involved in the synthesis of acrylic acid esters, starting with ethylene chlorohydrin, may be represented as follows:

(1) $CH_2OH.CH_2Cl + NaCN \longrightarrow CH_2OH.CH_2CN + NaCl.$

(2) $CH_2OH.CH_2CN + ROH + H_2SO_4 \longrightarrow$
$$CH_2=CH-COOR + NH_4HSO_4.$$
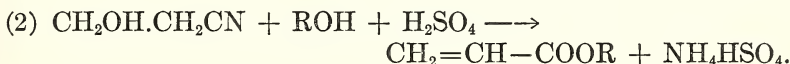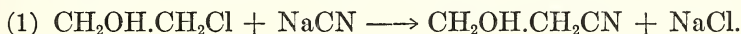
Esters of methacrylic acid are conveniently prepared by converting acetone cyanohydrin into $\alpha-$hydroxyisobutyric acid esters and

$$CH_3-\overset{\displaystyle OH}{\underset{\displaystyle CN}{C}}-CH_3$$
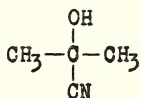
Acetone cyanohydrin

dehydrating the hydroxy ester with a suitable reagent, such as phosphorus trichloride or thionyl chloride. The esters of both acrylic and methacrylic acids polymerize under the influence of heat, light, oxygen, and oxygen-yielding substances, such as sodium peroxide, hydrogen peroxide, and benzoyl peroxide. The mechanism of the polymerization of polyacrylates is undoubtedly similar to that of other compounds containing vinyl groups. The polymers of the acrylates and methacrylates are characterized by colorless transparency, adhesive qualities, elasticity, and stability to light and heat. Their principal uses at present, such as the intermediate plastic layer in safety glass and as a substitute for glass in goggles and windshields, take advantage of the remarkable optical clarity of these resins. The trade name Acryloid is applied to the polymers of acrylic acid derivatives by one of the manufacturers in this country.

(d) POLYCHLOROPRENE

It will be noted that the chain molecules depicted above for the polymerization product of vinyl chloride do not have any residual unsaturated groups for cross linking of the various members. A vinyl compound which does contain such residual primary valences in the chain has been prepared from acetylene and the resultant polymerized product has marked flexibility. Acetylene in the presence of a saturated solution of ammonium and cuprous chlorides reacts to form vinylacetylene, which by the addition of hydrogen chloride yields chloroprene (2–chlorobutadiene–1,3):

$$2\ CH\equiv CH \xrightarrow[\substack{\text{and} \\ NH_4Cl}]{CuCl} CH\equiv C-CH=CH_2 \xrightarrow{+\ HCl} CH_2=CCl-CH=CH_2.$$

$$(x)$$
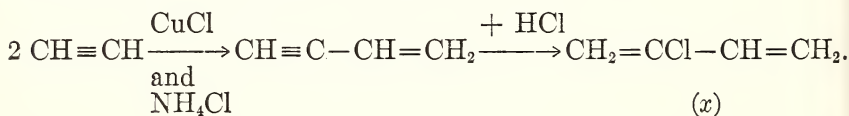
Combination of n such molecules (x) in a chain:

$$x-CH_2-CCl=CH-CH_2-CH_2-CCl=CH-CH_2-x_{n-3}.$$
$$(y)$$
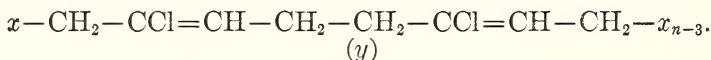
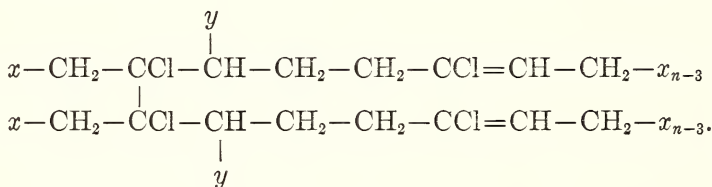Combination of such chains (y) by cross linkage:

$$\begin{array}{c} y \\ | \\ x-CH_2-CCl-CH-CH_2-CH_2-CCl=CH-CH_2-x_{n-3} \\ | \\ x-CH_2-CCl-CH-CH_2-CH_2-CCl=CH-CH_2-x_{n-3}. \\ | \\ y \end{array}$$

This is a theoretical picture of the formation of a synthetic rubber substitute on the market known as Duprene. Likewise isoprene, $CH_2=C(CH_3)-CH=CH_2$, which is assumed to be the monomer of natural rubber, is capable of forming chains bound together by cross linkages. It is a general rule that the chain polymers which still have a reactive group within the molecule, thereby permitting cross linkages, give rise to products characterized by flexibility, whereas polymers, which by further reaction, can only bring about the formation of longer chains, yield resins which tend to be hard and brittle.

Although polymerized chloroprene may be inferior to natural rubber in tensile strength and elastic extensibility at temperatures of 100° F or higher, its resistance to many chemicals and swelling agents which attack rubber is noteworthy. The relatively minor effect of mineral oils and gasoline is the basis of many practical uses of Duprene, such as hose, gaskets, and oil-resisting jackets for insulated cables. The high cost of production eliminates it from competition with rubber for most purposes, but the plentiful supply of raw materials essential to its production make it of considerable importance from the standpoint of national defense, as a substitute for the imported natural rubber.

4. HYDROXY-CARBOXYLIC RESINS

The hydroxy-carboxylic type of synthetic resin results from the production of comparatively large molecules by the esterification of polybasic acids with polyhydric alcohols. A simple example is the combination of phthalic acid with glycerol:

$$
\underset{\underset{O}{\overset{O}{\parallel}}{\underset{\parallel}{C}-OH}}{\bigcirc}{\overset{\parallel}{C}-OH} \; + \; \underset{CH_2OH}{\overset{CH_2OH}{\underset{\mid}{CHOH}}} \; \longrightarrow \; \underset{\underset{O}{\overset{O}{\parallel}}{C-O-CH_2}}{\bigcirc}{\overset{\parallel}{C}-OH} \; + \; H_2O
$$
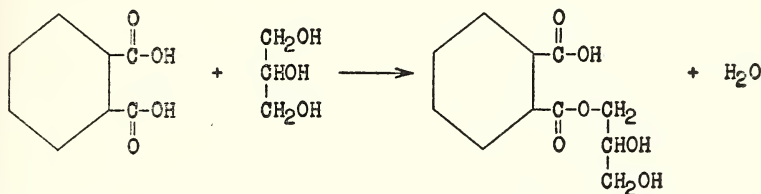
Further esterification of this product takes place at the free carboxyl and hydroxyl groups. In practice the reaction is carried out with phthalic anhydride and glycerol. Succinic acid, oleic acid, and the like are usually added to the reacting mixture to obtain flexible resins for varnish manufacture. The higher aliphatic polybasic acids containing six or more carbon atoms, such as adipic acid $HOOC$—$(CH_2)_4$—$COOH$, yield products with glycerol which are rubbery, plastic masses. They have been found very useful for plasticizing cellulose derivatives and phenolic resins. Other polyhydric alcohols may be used in place of or in conjunction with glycerol, such as ethylene glycol and diethylene glycol.

The synthetic resin industry is usually considered synonymous with plastic molding, but the hydroxy-carboxylic type is one of a number of synthetic resins which have found their chief use as film-forming bases in varnishes and lacquers. The synthetic resins have to a large extent supplanted the natural resins in such products, not because they could be produced more cheaply than the natural resins, but because they combine uniformity of material with valuable properties, such as flexibility, durability, and solubility in the usual varnish solvents. The hydroxy-carboxylic or alkyd (from alkyl-acid) resins may be utilized as either air-drying or baking coating materials. The A stage soluble resins are converted to C stage resins by heat treatment. Such finishes are characterized by excellent flexibility and tenacious adhesion.

Varnishes and enamels made from alkyd resins modified by the addition of drying oil to the reaction mixture are distinguished by rapidity of drying and good durability outdoors. The alkyd resins are also used in special cases as bonding agents for such fillers as mica, asbestos, and abrasives, when converted to the heat-hardened stage in hydraulic presses. These molded materials possess marked heat resistance, toughness, and electrical insulating qualities. Although these resins find very little use in custom molding, the fact that they rank second in quantity produced indicates their importance to the synthetic resin industry. They are known in the trade under such names as Glyptal and Rezyl.

5. INDENE RESINS

The indene resins are prepared from two compounds, indene and cumaron, and their homologs which are obtained from coal-tar
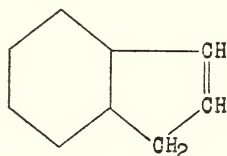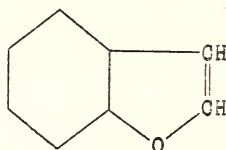
Indene   Cumaron

distillate. The solvent naphtha containing these substances is treated with a polymerizing agent such as sulphuric acid. The mechanism of the polymerization is considered to be essentially like that of the ethylene group in vinyl compounds. They are known as Cumar and Neville resins in this country and are used chiefly in varnishes, as rubber softeners, and as thermoplastic molding materials. The best grades of indene resins are light in color and free of acidity, but are brittle.

6. ORGANIC POLYSULPHIDES

Another synthetic plastic, radically different in composition from the products described above, results from the reaction of various dihalogenated organic compounds with alkaline polysulphides. Thus symmetrical-dichloroethane, commercially known as "ethylene dichloride", and sodium polysulphide yield a polysulphide derivative of ethane which, by curing at an elevated temperature in a manner similar to rubber vulcanization, forms a rubber-like material. The flexibility of the finished material depends upon the sulphur content; a polysulphide low in sulphur, such as the disulphide, yields a fairly stiff product, whereas the tetra- and pentasulphides give products which are very flexible. Other chlorinated paraffins can be used and the sodium polysulphide can be replaced by any alkali or alkaline earth polysulphide. Further modification of the process by the use of ethers and aryl halides has been proposed. The structure of the complex condensation product has not been determined, but the manifold opportunities for cross linking represented by the reactive polysulphide bonds satisfy the theoretical requirements set forth above for the production of a flexible material. Thus a possible formula for the polymer formed by the reaction of sodium tetrasulphide and dichloroethane may be constructed as follows:
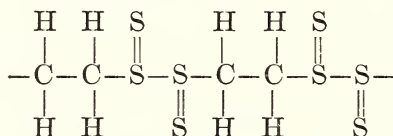
This synthetic rubber-like plastic is sold under the name Thiokol and has many applications where a flexible product resistant to gasoline, oil, organic solvents, and ozone is required. Among these may be mentioned gasoline hose lining, flexible covering for oil reservoirs, and protective sheathing for electric cables.

7. MISCELLANEOUS RESINS

There are a number of other synthetic resins which have appeared on the market within recent years and have potential industrial applications, particularly in synthetic finishes. Among these may be mentioned the petroleum-hydrocarbon, chlorinated diphenyl, and chlorinated rubber resins. The petroleum resins are produced by the catalytic polymerization of unsaturated distillates, which include both aliphatic and aromatic compounds. The chlorinated diphenyls are dependent upon the production of various isomeric polychloro derivatives of diphenyl for their resinous properties. They are known
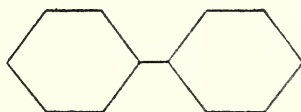
Diphenyl

commercially as Aroclors. The chlorinated rubber product is in a strict sense not a synthetic product; it is prepared by the chlorination of unvulcanized rubber. The industrial product is sold under the name Tornesite.

VII. NATURAL RESIN PLASTICS

The natural resins used in plastic compositions may be divided into three groups, the resins of animal origin, those of vegetable origin, and the asphalts, which are chiefly obtained from mineral sources.

1. ANIMAL RESINS

The only resin of industrial importance in the first group is shellac. This material is produced by an insect which grows parasitically upon certain species of trees in India and southern Asia. Organic matter obtained from the tree is converted by the female into a lac with which she protects her eggs. The chemical structure of shellac has not been fully determined. The high saponification value and low acid number, however, lead to the conclusion that it is an ester. The base has not been isolated. One of the principal acidic constituents has been found to be aleuritic acid,

$$CH_2OH(CH_2)_5(CHOH)_2(CH_2)_7COOH.$$

There is evidence that shellac is a lactide condensation product of various complex hydroxy-carboxylic acids such as the above. Such condensation products are formed by the splitting out of water by reaction between an alcoholic group of one molecule and the acid group of another. They are to be distinguished from lactone condensation products, which are formed by the reaction between these two groups within one molecule. In addition to its well-known use as a spirit varnish finish, shellac is an important constituent of many proprietary organic molding compositions.

2. VEGETABLE RESINS

The natural resins of vegetable origin are obtained from various trees. Those of one group have become fossilized and are obtained from the earth or the beds of lakes and streams. The melting points of these resins vary from 75 to 450° C (167 to 842° F); copal and amber are members of this group. Another group is derived from living trees. Two examples of this type are dammar gum which is obtained in Java and Sumatra, and rosin which is the solid residue left in the still after distillation of turpentine from pine resin extracts in this country. These products melt more readily than the fossil resins, generally between 75 and 100° C (167 and 212° F). Studies of the structures of these resins indicate that they consist of complex terpenic acids and esters together with some hydrocarbons. Thus rosin consists largely of abietic acid $C_{19}H_{29}COOH$, for which the formula
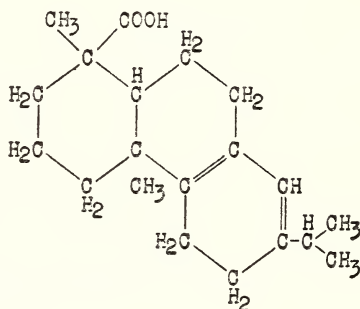
has been proposed. These natural resins of vegetable origin are used in various organic molding compositions. The product of esterification of rosin with glycerol is known as ester gum and has had extensive use in the varnish industry.

3. MINERAL RESINS

The asphalts comprise the third group of the natural resins and are sometimes called the mineral resins. They consist of naturally occurring hydrocarbon complexes, termed bitumens, which are insoluble in water but soluble in carbon disulphide and benzene. They are generally black in color, hard at ordinary temperature, viscous at about 70° C (158° F) and melt at about 100° C (212° F). They are obtained from mineral deposits in various parts of the world, including many in this country. Closely related to the asphalts are the tars and pitches which may be obtained naturally or are formed by the distillation of asphaltic petroleum. The chemistry of these bituminous substances is essentially a study of hydrocarbon compounds of high molecular weight, containing members of both the aliphatic and aromatic series.

4. NATURAL WAXES

It is interesting to note that the natural waxes, which are softer and melt at lower temperatures than the resins, may also be classified according to their sources as animal (beeswax), vegetable (carnauba

wax from the leaves of a Brazilian pine) and mineral (montan wax from peat and brown coal). These products are quite similar chemically and consist largely of fatty acid esters of mono- and dihydric alcohols mixed with the related free acids, alcohols, and hydrocarbons. The number of carbon atoms per molecule in these compounds varies from approximately 25 to 60. Waxes obtained from mineral sources also include the fossil waxes such as ozokerite (from which ceresin is obtained by a refining process) and petroleum waxes such as paraffin. These materials differ from the true waxes (saponifiable), listed above, in chemical composition, and consist of mixtures of saturated hydrocarbons. The natural waxes are used as ingredients of floor waxes, polishes, paper coatings, leather finishes, electrical insulation compositions, and phonograph records, and for waterproofing textiles and wood. The waxes are often employed in plastic compositions in admixture with the natural resins in order to obtain the requisite consistency for molding or casting at low temperatures.

VIII. CELLULOSE PLASTICS

The use of cellulose derivatives in the plastics industry was in the early stages practically confined to the nitrate product. Today, however, the xanthate and acetate derivatives figure prominently in this field, and there are many other cellulose compounds which are in the experimental and semicommercial stages. The chief sources of cellulose are cotton and wood. Chemically cellulose is made up of long chain molecules in which the unit $C_6H_{10}O_5$ is repeated many times. For simplicity and to obtain a clearer picture of the behavior of this molecule it may be represented, without attempting to indicate the steric structure, as glucose anhydride:
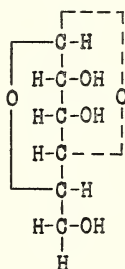

although it should be understood that in cellulose the five-membered oxygen ring indicated by the broken lines does not occur, but rather that the carbon atoms of this ring which are attached to oxygen are linked to other such units through intervening oxygen atoms. One suggested formula for the chemical structure of cellulose is shown below:
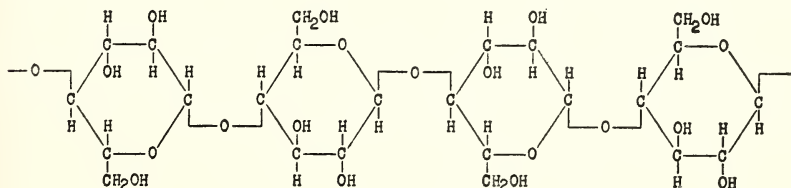
The unit molecule, $C_6H_{10}O_5$, it will be noted, has three hydroxyl groups, and these lend themselves readily to esterification.

1. CELLULOSE NITRATE

In the preparation of cellulose nitrate, purified cellulose is treated with nitric acid and a dehydrating agent such as concentrated sulphuric acid to take up the water that is formed:
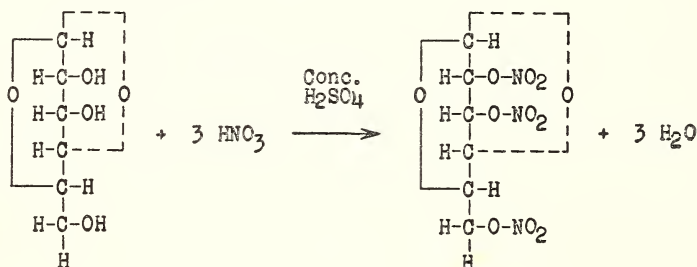
It should be observed that this is an ester; that is, the nitrogen is connected to oxygen rather than to carbon as in trinitrotoluene:
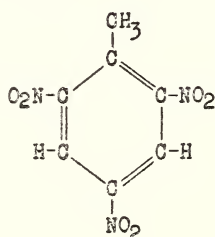
The term "nitrocellulose" is a misnomer. In practice the trinitrate is not prepared for use in plastics as it yields brittle and unstable products. A compound of lower nitrogen content is made instead by the use of a suitable nitrating mixture of nitric and sulphuric acids.

The preparation of cellulose nitrate for plastic manufacture involves (1) chemical treatment of the cellulosic raw material to bring it to the proper purity, molecular simplicity, and physical condition for intimate contact of the fibers and nitrating medium; (2) immersion of this cellulose in an acid mixture correctly adjusted in sulphuric acid, nitric acid, and water content to give the desired degree of nitration; (3) adequate control of the temperature and time of contact of the cellulose with the acid; (4) removal of the spent acid mixture by hydraulic pressure or centrifuging; (5) "drowning" the residual mass in a large volume of water to minimize any local rise of temperature; and (6) removal of any remaining free acid and unstable esters by boiling the nitrated cellulose with dilute acid and, finally, with water. The cellulose nitrate so prepared is mixed with solvents such as alcohol, alcohol-ether blend or acetone, and a plasticizer, for example, camphor. Dyes and pigments are added and the plastic mass, sometimes called pyroxylin, is formed into tubes, rods, and sheets by suit-

able hydraulic presses. The processing equipment includes sawing, die- or punch-blanking, and beveling apparatus, and heated presses for stretching and forming operations.
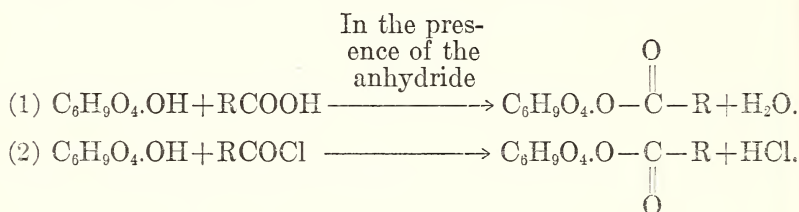
Cellulose nitrate is a true thermoplastic material, that is, it softens when heated and hardens again when cooled. Its ease of molding, the many methods by which it may be worked, and the infinite variety of colors and mottled effects in which it may be obtained are important factors in its extensive use. The readiness with which parts may be cemented together or to other materials is also noteworthy. Its low ignition temperature and high rate of burning are, however, serious disadvantages.

Pyroxylin plastics are used in the fabrication of combs and brushes of all kinds, hand mirrors, trinket boxes, ping-pong balls, fountain pen barrels, and myriads of other articles in everyday use. Hollow toys are made either by molding the two halves and sticking them together at the edges by heat or cement, or by forcing air between two thin sheets of the plastic, previously heated on a steam table. It should be noted that cellulose nitrate plastics are never to be heated over or near a flame. A considerable quantity of pyroxylin plastic is used for covering the heels of ladies' shoes. Cellulose nitrate also finds an application in the shoe industry as the binder used to cement on sole leather, eliminating the necessity of nailing or stitching operations. So-called liquid or cold solder consists of plasticized cellulose nitrate dissolved in suitable solvents and mixed with aluminum powder to give a metallic appearance. Both the solvents and the dried plastic are highly flammable and should be kept away from a flame. These cements are not satisfactory for repairing kitchen utensils because heat will decompose them and water will cause them to become loose from metals. Another product of this type is made by mixing cellulose nitrate with wood flour and is known commercially as Plastic Wood. The cellulose nitrate and a plasticizing agent, such as camphor, are dissolved in acetone, ethyl acetate, or other solvent or solvent blend, and mixed with finely ground sawdust. When exposed to the air the acetone evaporates, leaving a hard product simulating wood. Toluene may be added to the solvent to prevent too rapid drying. The manufacture of motion-picture films takes a large quantity of cellulose nitrate, which forms a tough, transparent vehicle for the photographic gelatin emulsion. Cellulose nitrate is also used in a highly plasticized state in the manufacture of artificial leather. Camphor, castor oil, or other suitable chemicals are employed as plasticizers and the plastic mass is applied to cotton cloth. The finished product is used for bookbindings, furniture upholstery, and the like. Some of the trade names of cellulose nitrate plastics include Celluloid, Fiberloid, Nixonoid, and Pyralin.

2. CELLULOSE ACETATE AND OTHER ESTERS

Cellulose acetate is prepared by the esterification of cellulose with glacial acetic acid, using some acetic anhydride to combine with the water formed by the action of the acetic acid on the cellulose and a small amount of sulphuric acid to catalyze the reaction. In this case it is found necessary to prepare the triacetate and hydrolyze that

compound to a product which is more suitable for use in plastics, because of a lower acetyl content and greater solubility in common solvents. The general methods for the preparation of this and other cellulose esters, such as the propionate and butyrate, by reaction with acid anhydrides or acid chlorides may be represented as follows:

$$
\text{In the presence of the anhydride}
$$

$$
(1)\ C_6H_9O_4.OH + RCOOH \xrightarrow{\hspace{2cm}} C_6H_9O_4.O-\overset{\displaystyle O}{\overset{\|}{C}}-R + H_2O.
$$

$$
(2)\ C_6H_9O_4.OH + RCOCl \xrightarrow{\hspace{2cm}} C_6H_9O_4.O-\underset{\displaystyle O}{\underset{\|}{C}}-R + HCl.
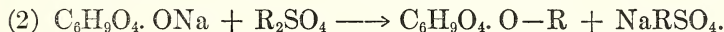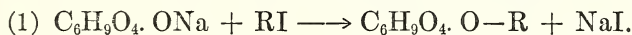$$

The molding procedure for these products is similar to that described for cellulose nitrate. Cellulose acetate plastics resemble the nitrate products in physical properties, with the notable exceptions of flammability and stability. They burn very slowly and have a comparatively high ignition temperature. They are highly resistant to embrittlement and discoloration by aging, especially on exposure to sunlight. All ranges of color and of light transmission from transparency through translucency to opacity may be obtained.

Many products formerly molded of cellulose nitrate are now being fabricated with cellulose acetate, although there is still a price differential of approximately ten percent in favor of the nitrate material. Thin sheets of cellulose acetate are used as transparent wrapping paper, known as Kodapak. Safety photographic film for home and hospital use is also made from this cellulose derivative. Its use in the manufacture of acetate rayon under the trade name Celanese is well known. One of the important uses of cellulose acetate is in the manufacture of safety glass. Cellulose nitrate was at first used for this purpose, but has been largely replaced by cellulose acetate because the latter is superior in resistance to deterioration by sunlight. In the manufacture of safety glass, a thin sheet of plasticized cellulose acetate is sandwiched between two sheets of plate glass which have been covered with a suitable bonding agent. The whole assembly is firmly cemented together by the application of heat and pressure. It is necessary to seal the edges of such laminated glass with a thermoplastic weatherproof pitch product to prevent deterioration of the cellulose acetate because of absorption of water or leeching out of plasticizer.

Another type of safety glass, called Plexite, is now on the market, in which the plastic layer consists of an acrylate resin. A solution of this resin is flowed on to the glass and run through a dryer before pressing. No additional cementing agents or edge-sealing treatments are necessary with this resin plastic. Transparent sheets of cellulose acetate are also commonly used without glass on aircraft, as curved windshields which offer minimum wind resistance. Their relatively lightweight and flexibility have been important factors in this development. Cellulose acetate plastics are sold under such trade names as Lumarith, Fiberloid, Plastacele, and Tenite.

3. CELLULOSE ETHERS

Various cellulose ethers have appeared on the market within the past few years, notably benzylcellulose and ethylcellulose. The preparation of these derivatives from alkyl halides and alkyl sulphates may be carried out according to the following reactions:

(1) $C_6H_9O_4.ONa + RI \longrightarrow C_6H_9O_4.O-R + NaI.$

(2) $C_6H_9O_4.ONa + R_2SO_4 \longrightarrow C_6H_9O_4.O-R + NaRSO_4.$

The cellulose ether plastics have not yet been produced commercially in this country.

4. REGENERATED CELLULOSE

Another cellulose plastic which has become an important item of commerce is the transparent wrapping material known as Cellophane and Sylphrap. The chemical composition of the finished product is similar to that of the original cellulose, but in the process of manufacture, sodium cellulose xanthate is first prepared and the cellulose is then regenerated by suitable chemical treatment. The chemical reactions involved may be briefly summarized.

(1) Sodium cellulose is prepared by treatment of the wood pulp or cotton linters with an 18 to 20-percent sodium hydroxide solution. There is some question whether this alkali reacts with the hydroxyl group in the manner of formation of a sodium alcoholate, or whether it is merely loosely combined as in the case of water of crystallization. Its primary action is the overcoming of the cohesion forces holding together the cellulose fibrils, with an accompanying increase in reactivity. The reaction as originally written by Cross and Bevan is as follows:

$$(C_6H_9O_4.OH)_n + n\,NaOH \longrightarrow (C_6H_9O_4.ONa)_n + n\,H_2O.$$
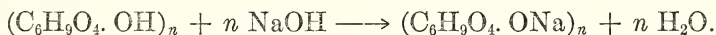
Most of the excess alkali is removed by a pressing operation.

(2) The sodium cellulose reacts with carbon disulphide to yield sodium cellulose xanthate:

$$C_6H_9O_4.ONa + CS_2 \longrightarrow C_6H_9O_4.O-\overset{\overset{\textstyle S}{\|}}{C}-S-Na.$$
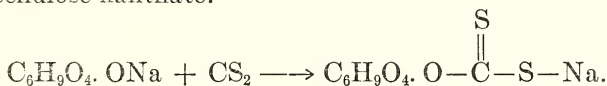
(3) This product is dissolved in dilute sodium hydroxide to yield an orange-colored sirupy mass, known technically as viscose. After a ripening period, the viscose is forced through narrow slots into a bath containing a solution of sulphuric acid and sodium sulphate, which brings about coagulation and regeneration of the cellulose:

$$C_6H_9O_4.O-\underset{\underset{\textstyle S}{\|}}{C}-S-Na + H_2SO_4 \longrightarrow C_6H_9O_4.OH + CS_2 + NaHSO_4.$$
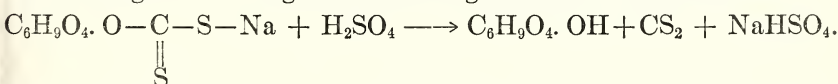
The product can not be dissolved in organic solvents such as are useful in the case of cellulose nitrate and cellulose acetate. For many purposes, it is imperative that the passage of moisture through the film be inhibited. To accomplish this, the regenerated cellulose is coated with a thin film of cellulose nitrate lacquer. In addition to its use in the production of transparent sheets, this xanthate method of processing cellulose is also employed in the manufacture of viscose rayon.

IX. PROTEIN PLASTICS

The fourth and final group of the organic plastics to be considered comprises the protein materials. The best known of these plastics are made from casein, obtained from milk. Other types that are sometimes used include the blood albumins obtained as by-products of slaughterhouse operations and the soy-bean proteins which remain in the pressed cake after removal of the oil. These proteins must be converted into hard and stable compounds in order to make them into useful articles. There are a variety of substances which have been proposed for this purpose, such as aldehydes, chromium salts, tannic acid, and the like. In practice, formaldehyde is universally used to harden these protein plastics. The exact nature of the reaction which takes place is not known but there is probably a condensation of the aldehyde with the amino group. If the complex protein molecule be represented by di-alanine, containing a single peptide linkage, the condensation reaction may be written thus:

$$CH_3-\underset{\underset{COOH}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-NH_2 + CH_2O \longrightarrow$$

$$CH_3-\underset{\underset{COOH}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-N=CH_2 + H_2O$$
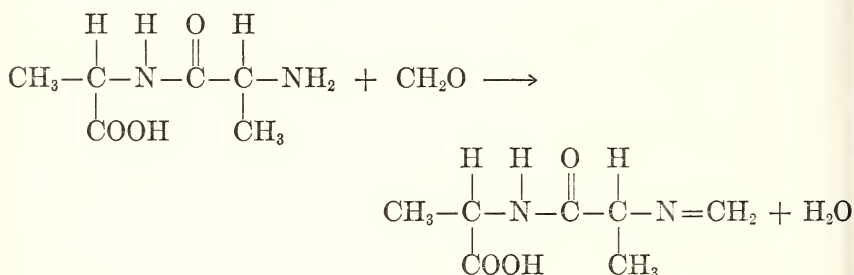
The following description of the manufacturing process for casein plastics applies to the other protein materials as well. Casein obtained by the action of the enzyme, rennet, on milk is generally preferred as the raw material. This is ground on a mill with corrugated rolls or by an impact pulverizer to a suitable fineness. It is then thoroughly mixed with dyes, plasticizers such as glycerol, acetanilide, or the like, and a small amount of water in a special dough mixer. After this latter operation, the mixture must be carried through the next steps without delay. It is fed into heated hydraulic presses for the production of sheets, or into a heated cylinder press fitted with a rotating screw and a nozzle with a bore of the desired size for the production of rods and tubes. The sheets, rods, and tubes so formed are placed in tanks, where they are hardened by immersion in aqueous formaldehyde solution for periods varying from two weeks to several months, depending upon the thickness of the material. The excess moisture is then allowed to evaporate slowly in order to minimize warping. This outline of the process is intended to give only a general picture of the preparation of casein plastics, and no attempt has been made to include necessary precautions and details of chemical control that are required during their manufacture. Casein plastics are sold in this country under such trade names as Ameroid, Ronyx, and Aladdinite. They are used in the manufacture of buttons, buckles, beads, and various novelty articles. Their property of taking up considerable amounts of moisture at high relative humidities have made them unsuitable for outdoor use.

X. PLASTICS TRADE STATISTICS

Statistics compiled by the United States Tariff Commission and the Bureau of the Census, on the production and sales value of plastic products during 1934, are presented in table 1 to indicate the relative cost and industrial importance of various types of organic plastics.

TABLE 1.—*Plastics trade statistics*

Product	Total production	Sales			Year
		Quantity	Value	Unit value	
	Pounds	*Pounds*	*Dollars*	*Dollars*	
Derived from phenol_____	24, 890, 000	23, 201, 000	5, 233, 000	0. 23	1934
Cast products derived from phenol_____	4, 968, 000	4, 794, 000	2, 099, 000	. 44	1934
Derived from cresol and/or phenol_____	10, 887, 000	8, 091, 000	1, 705, 000	. 21	1934
Derived from phthalic anhydride_____	14, 877, 000	7, 085, 000	1, 022, 000	. 14	1934
Derived from maleic acid, styrol, or xylenol_____	177, 000	180, 000	67, 000	. 36	1934
Derived from urea or thiourea_____	3, 471, 000	3, 116, 000	1, 291, 000	. 41	1934
Miscellaneous resins of non-coal-tar origin (vinyl, petroleum, etc.)_____		442, 000	225, 000	. 51	1934
Cellulose nitrate_____	12, 934, 569	10, 085, 046	7, 799, 283	. 77	1933
Cellulose acetate_____	4, 826, 347	4, 633, 054		(a)	1934
Casein (imports only; domestic figures not available)_____		13, 264	4, 981	. 38	1933

a Approximately 10 percent higher than cellulose nitrate.

XI. SOURCES OF ADDITIONAL INFORMATION ON PLASTICS

Detailed information concerning the mechanical, electrical, thermal, optical, and chemical properties of the various organic plastics is available in the literature. Considerable data on the properties and uses of these materials are also contained in descriptive bulletins published by the manufacturers. The following references are suggested for the reader who wishes to obtain further information on special phases of this subject.

1. PUBLICATIONS OF THE NATIONAL BUREAU OF STANDARDS [2]

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G. M. Kline, *Transparent plastics for aircraft windows.* Ind. Eng. Chem., News Ed. **13,** 479 (Dec. 20, 1935); Modern Plastics **13,** no. 5, 17 (January 1936).

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J. W. McBurney, *Indentation of asphalt tile.* Proc. ASTM **34,** II, 591 (1934).

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T. P. Sager, *Rubber substitutes as coatings for balloon fabrics.* J. Aero. Sci. **3,** 63 (1935).

[2] The prices of Government publications are indicated. These papers can be obtained from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C.

2. MANUFACTURERS' BULLETINS

American Catalin Corporation, 1 Park Avenue, New York, N. Y. *Catalin— Its characteristics, weights, and working methods.*

American Cyanamid Co., 30 Rockefeller Plaza, New York, N. Y. *Rezyls and Teglacs.*

American Plastics Corporation, 50 Union Square, New York, N. Y. *Karolith— A casein plastic.*

Bakelite Corporation, 247 Park Avenue, New York, N. Y. *Bakelite molded; Bakelite laminated; Bakelite cast resins; Bakelite heat-hardenable varnish, enamel, lacquer, and cement.*

Barrett Co., 40 Rector Street, New York, N. Y. *Cumar resins.*

Beetleware Division, American Cyanamid Co., 49 West Forty-ninth Street, New York, N. Y. *Beetle.*

Boonton Molding Co., Boonton, N. J. *A ready reference for plastics.*

A. S. Boyle Co., 1934 Dana Avenue, Cincinnati, Ohio. *Things to do with Plastic Wood.*

Carbide and Carbon Chemicals Corporation, 30 East Forty-second Street, New York, N. Y. *Vinylite resins.*

Celluloid Corporation, 10 East Fortieth Street, New York, N. Y. *Lumarith.*

Continental-Diamond Fibre Co., Newark, Del. *Dilecto—A laminated phenolic material.*

Cutler-Hammer, Inc., Twelfth and St. Paul Avenue, Milwaukee, Wis. *Come adventuring (Thermoplax).*

E. I. du Pont de Nemours and Co., Inc., Wilmington, Del. *The Duprene manual.*

Du Pont Viscoloid Co., Arlington, N. J. *Pyralin—Its manufacture and use.*

Durite Plastics, Division of Stokes and Smith Co., Summerdale Avenue near Roosevelt Boulevard, Philadelphia, Pa. *Durite.*

Formica Insulation Co., 4614 Spring Grove Avenue, Cincinnati, Ohio. *What Formica is.*

Garfield Manufacturing Co., Garfield, N. J. *Why Gummon.*

General Electric Corporation, Plastics Department, 920 West Avenue, Lynn, Mass. *Bulletin GEA 1457 (Glyptal, Textolite, Cetec).*

General Plastics Inc., North Tonawanda, N. Y. *Do it with Durez.*

Glyco Products Co., Inc., 949 Broadway, New York, N. Y. *Chemicals by Glyco.*

Haveg Corporation, Newark, Del. *Haveg corrosion-resistant chemical equipment.*

Hercules Powder Co., Wilmington, Del. *Hercose C; Cellulose nitroacetate.*

Makalot Corporation, 262 Washington Street, Boston, Mass. *Makalot.*

Neville Co., Neville Island Post Office, Pittsburgh, Pa. *Neville resin.*

Plaskon Co., Inc., 2121 Sylvan Avenue, Toledo, Ohio. *Plaskon.*

Resinous Products and Chemical Co., Inc., 222 West Washington Square, Philadelphia, Pa. *Paraplex.*

Resinox Corporation, New York Central Building, New York, N. Y. *Resinox.*

Shawinigan Products Corporation, Shawinigan Falls, Quebec, Canada. *Gelva, Alvar, and Formvar.*

F. J. Stokes Machine Co., Olney Post Office, Philadelphia, Pa. *Equipment for the process industries.*

Swann Chemical Co., Birmingham, Ala. *A brief description of the Aroclors.*

Tennessee Eastman Corporation, Kingsport, Tenn. *Tenite.*

Thiokol Corporation, Yardville, N. J. *What Thiokol is doing for industry.*

Unyte Corporation, 521 Fifth Avenue, New York, N. Y. *Unyte.*

Watson-Stillman Co., 109 Aldene Road, Roselle, N. J. *Hydraulic plastic molding machinery.*

Wm. Zinsser and Co., Inc., 516 West Fifty-ninth Street, New York, N. Y. *The story of shellac.*

3. TRADE JOURNALS

British Plastics and Molded Products Trader. (Plastics Press, Limited, 19–23 Ludgate Hill, London, E. C.4, England).

Kunststoffe. (J. F. Lehmanns Verlag, Munich 2 SW, Paul Heyse-Strasse 26, Germany.)

Modern Plastics. (Breskin and Charlton Publishing Corporation, 425 Fourth Avenue, New York, N. Y.)

Plastische massen in wissenschaft und technik. (Cologne, Germany.)

Revue Générale des Matières Plastiques. (61, Avenue Jean-Jaurès, Paris, France.)

4. BOOKS

A. Abraham, Asphalts and Allied Substances. 606 p. (D. Van Nostrand Co., New York, 1918.)

C. Dorée, The Methods of Cellulose Chemistry. 499 p. (Chapman and Hall, Ltd., London, 1933.)

C. Ellis, The Chemistry of Synthetic Resins. 2 vols., 1626 p. (Reinhold Publishing Corporation, New York, 1935.)

T. Hedley, A. A. Drummond, and R. S. Morrell, The Chemistry of the Natural and Synthetic Resins. 196 p. (D. Van Nostrand Co., New York, 1927.)

E. Hemming, Plastics and Molded Electrical Insulation. 313 p. (Reinhold Publishing Corporation, New York, 1923.)

J. I. Lewkowitsch, Chemical Technology and Analysis of Oils, Fats, and Waxes. 6th ed., 3 vol. (Macmillan and Co., Ltd., London, 1921–23.)

L. F. Rahm, Plastic Molding. An introduction to the materials, equipment, and methods used in the fabrication of plastic products. 246 p. (McGraw-Hill Book Co., Incorporated, New York, 1933.)

J. Scheiber, and K. Sandig, Artificial Resins (translation by E. Fyleman). 447 p. (Sir Isaac Pitman and Sons, Ltd., London, 1931.)

E. Sutermeister, Casein and Its Industrial Applications. 296 p. (Reinhold Publishing Corporation, New York, 1927.)

E. C. Worden, The Technology of Cellulose Esters. Vols. 1 (5 pts.) and 8. (D. Van Nostrand Co., New York, 1916.)

E. C. Worden, The Technology of Cellulose Ethers. 5 vol. (Worden Laboratory and Library, Millburn, N. J., 1933.)

5. LITERATURE ON PROPERTIES, TRADE NAMES, AND TRADE STATISTICS

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