HANDBOOK OF PLASTICS

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flexural and impact strengths. However, it does appear suitable for uses where mechanical properties are distinctly secondary to electrical properties and heat distortion temperature. It is being considered for specialty items in coil forms, cable connector parts, switch parts, coaxial cable spacers, stand-off insulators, etc.

The data herein reported are based on information developed in the laboratories of the General Aniline and Film Corporation.

Polyvinyl Chloride

Polyvinyl chloride is available as a granular powder, plasticized sheets, extruded tubes, and special shapes. Normally it is a rigid material and is highly plasticized for most uses.

It is a nonflammable resin, practically insoluble at ordinary temperatures. It is moisture resistant, nontoxic, odorless, and tasteless. Straight polyvinyl chloride is almost fusible and, accordingly, is very difficult to fabricate. Combined with proper plasticizers, however, it is a very versatile plastic.

Polyvinyl chloride may be molded at temperatures from 225° to 275° F. and pressures from 1000 to 2000 psi.

Sheets and Pipes. Clear sheets of polyvinyl chloride can be made. Commercial pipes and pipe fittings are made of rigid polyvinyl chloride compounds, i.e., slightly plasticized resin. They are light, strong, and can be heat-sealed or shaped.

Polyvinyl chloride is used for packaging because of its physical properties, heat-sealability, and good moisture resistance.

Extruded Forms. One of the most recent and widest uses for polyvinyl chloride is as highly plasticized, extruded wire coverings providing electrical insulation and waterproofness for electric wires.

Extruded polyvinyl chloride is gaining considerable popularity as a reinforcing agent in concrete. The fiber has great strength, is light in weight, resistant to water, alkalies, acids, and rust, and has good insulating properties. Plasticized polyvinyl chloride is extruded as cable coverings and calendered in the form of tape.

Bristles and textile fibers of polyvinyl chloride are extruded. Polyvinyl chloride bristles for brushes resist moisture, alcohol, gasoline, and many other chemicals.

Coatings. This vinyl material is used occasionally for chemical plant construction of cooling coils, ball floats, and valve balls. Iron tanks are coated internally with the same material in foil form. It is stable to acids, alkalies, and salt soltions, may be safely used at a temperature of 60°.C. (140° F.), and is nonflammable.

Polyvinyl chloride is used for tank linings and fabric coatings. Solutions of the plasticized resin are used in special types of varnishes. Polyvinyl chloride is used in a cloth-coating preparation to make artificial leather.

Vinyl Chloride-acetate Copolymers

Products of the conjoint polymerization of vinyl chloride and vinyl acetate, this family of resins includes several grades varying in vinyl chloride content from 85 to 95%, and in molecular weight. The various grades are manufactured to cover an extensive range of diverse methods of fabrication and fields of use.

As made, the resins are fine white powders which, in molded form, show excellent clarity and only slight inherent color. Hence they offer an unlimited range of

color possibilities. Having very low moisture absorption, these resins may be fabricated into forms which are characterized by exceptional dimensional stability. Other desirable properties include good electrical properties, toughness, high modulus of elasticity (rigidity), low mold shrinkage, nonflammability, freedom from taste and odor, chemical inertness, including resistance to acids, alkalies, alcohols, and many other chemicals, and ease of fabrication and machining.

Vinyl chloride-acetate resin usages may be divided into two broad classes, comprising rigid and nonrigid or elastomeric forms. Compounded and fabricated without the addition of plasticizer these resins are hard and rigid; by compounding with plasticizer, such as dioctyl phthalate, they are transformed into resilient, rubberlike materials of almost any desired degree of stiffness. Unlimited colors are available in both types and the inherent desirable properties of the resins themselves are largely retained in both the rigid and elastomeric fabricated forms.

The rigid materials are ordinarily based on resin of 85 to 90% vinyl chloride content. As molding materials, they find extensive use in lightweight printing plates, phonograph records, injection molding compounds for combs, closures, and special molding applications requiring extraordinary chemical resistance. Rigid materials are also available in calendered and film form, in cast films of 1 to 5 mils thickness, and in calendered (up to 15 mils in thickness), press polish, matte, or press-matte finishes in 10 to 150 mils thickness. Standard pressed sheet size is 20 by 50 in. Vinyl chloride-acetate rigid sheet and film have found extensive use for book bindings, drawn or swaged radio escutcheons, wrist watch and gage crystals, aircraft glazing, template stock for the automotive and aircraft trade, navigating and computing instruments, transparent packages, etc.

Extensive as are the uses for vinyl chloride-acetate rigid materials (which are generally predicated on resin of 90% vinyl chloride content or greater), the elastomeric varieties have established even wider fields of application. The greater latitude of employment of the elastomeric forms derives from the fact that any of numerous plasticizers or combinations thereof may be added to the resin to impart a range of hardness and stiffness values and other specific properties. Certain plasticizers, for instance, provide compounds which, although tough, rubbery and nontacky at 170° F., are still flexible at temperatures as low as −60° F. Vinyl chloride-acetate elastomers have found use for such purposes as upholstery coating, calendered and solution-coated proofed goods, various types of extruded insulation, shoe soles and uppers, injection molded and extruded automotive grommets and window channeling, aircraft conduit tubing, water bags fabricated from heat-sealed calendered sheeting, shower curtains and baby pants from unsupported calendered film or from fabric coated by dry calendering or solution methods. Amenable to fabrication by calendering, including fabric coating, film casting, molding, extrusion, solution coating and heat sealing, there are literally thousands of applications for this versatile family of materials.

A relatively new form of the vinyl chloride-acetate resin elastomers are the materials known as plastisols. Available in all colors, these products are pourable liquids comprising dispersions of resins in plasticizer which, when heated to about 160° C. for 10 min., convert to solid elastomeric masses having properties

approaching those obtained by equivalent dry compounded materials. The plastisols have found extensive use for sealing electrical cable against the passage of water and their liquid form, which connotes moldability under very low pressures, adapt them well for industrial uses and toy and novelty goods.

Another new form of the vinyl chloride-acetate resins comprises the organosols. These liquid materials are dispersions of resin and plasticizer in low-cost solvent-non-solvent mixtures. The suspending medium being primarily low-cost hydrocarbon, the economy, for solution application purposes, over conventional solutions based on relatively high priced solvents is obvious. The organosols have found extensive use for fabric, foil, and paper coatings.

Extruded Forms. Vinyl chloride-acetate plastics are extruded in a variety of shapes and as electrical insulation. The newest development is the extrustion of minute fibers to form a synthetic yarn woven into a new fabric—Vinyon. This process and the resultant material are described at length under Multifilaments, page 452.

TABLE 5.7. PROPERTIES OF EXTRUDED VINYL CHLORIDE–ACETATE

Yarn	Dry (relative humidity 65%)		Wet	
	Tenacity Gm./denier	Elongation %	Tenacity Gm./denier	Elongation %
Silk (degummed)	4.22	16	3.4	26.3
Viscose rayon	2.00	18	1.0	25
Acetate rayon	1.40	27	0.85	36
Vinyon:				
High stretch	—	—	4.00	18
Medium stretch	—	—	2.30	25
Unstretched	—	—	1.00	120

Vinyon fish nets and lines tried along the Florida coast are reported to have caught twice as many fish as the ordinary tar-impregnated cotton nets and showed no signs of deterioration after six months although all other types showed partial or complete disintegration.

Other suggested uses for the new material are: shower curtains, bathing suits, waterproof acid- and alkali-resistant clothing, full-fashioned hosiery, fireproof awnings, curtain, sail cloth, umbrella fabrics, tent and tarpaulin materials, shoe linings, braids and various knit fabrics.

Coatings. Vinyl chloride-acetate resins find wide use in surface coatings. In general, those high in vinyl acetate are better lacquer ingredients than those high in vinyl chloride.

Two types of resins used in surface coatings are as follows:

1. A resin of low molecular weight, containing 85 to 88% chloride, used in coating paper, in lacquers, and in floor tile.
2. A resin of low molecular weight, compatible with nitrocellulose and used in lacquers and finishes for industrial applications.

In lacquers these resins give high resistance to water, oils, and chemicals. Drying is by evaporation rather than by oxidation. They are suitable for lining food containers, coating concrete, coating metal, lining plating tanks, coating

paper for bottle cap liners, and making wallboard coatings. The most successful application at present is as an inside coating for beer cans. Also metal primers.

Vinyl chloride-acetate coatings are used extensively as finishes for sheet metal. Their exceptional toughness and flexibility make them especially well suited for this, as metal stock is often punched, spun, drawn, or otherwise fabricated after coating; nontoxic finishes, free from taste and odor, result. The coatings usually are baked at a relatively high temperature to secure the proper adherence. The coatings have unusual resistance to moisture, grease, alcohol, acids, alkalies, and most other reagents. These properties explain the present wide use and rapidly increasing demand for finishes made from them.

The solvents are primarily ketones or mixtures of ketones and coal-tar hydrocarbons. The required proportion of ketone to hydrocarbon depends on the concentration of the resin in solution and is determined by the viscosity characteristics of the resin solutions. At relatively low concentrations (8 to 10%), very lean thinner mixtures may be employed, but higher solids requirements need a greater proportion of ketone.

The resins are neutral, chemically inert, and not compatible with nitrocellulose or other resins or drying oils, hence in surface coatings they are the only film-forming constituents. They have high internal plasticity, permitting the incorporation and use of a large number of different types of fillers and pigments. They darken on exposure to direct sunlight or heat, but this is lessened by the incorporation of 1 or 2% of stabilizers such as lead stearate, lead oleate, calcium stearate, slaked lime, or somewhat larger proportions of the commonly used lead pigments. The stabilizers should be added to the powdered resin before fluxing on the mill or in an internal mixer. Where flexibility is a factor, plasticizers such as dibutyl Cellosolve phthalate, dibutyl phthalate, tricresyl phosphate, and Santicizer B-16 are recommended. The amount added depends on the degree of flexibility desired.

The resin itself is supplied as a white, fluffy powder, yielding transparent, translucent, or opaque coatings in many shades and tints. It is soluble in ketones and related compounds, esters, chlorinated hydrocarbons, dioxane, propylene oxide, and mesityl oxide. It swells or dissolves in dichloroethyl ether and in aromatic hydrocarbons.

The presence of pigments, wax, stabilizers, and the like in filled compounds or coatings generally decreases the resistance to chemicals and solvents. Baking at a high temperature generally makes surface coatings of polyvinyl chloride-acetate resin less suscepitble to attack by solvents.

Impregnating Liquids. Vinyl chloride-acetate impregnating varnishes are used for impregnating paper, felt, and various fabrics. Since the resin is thermoplastic, fabrics impregnated with it may be formed by heat and pressure into shapes which they will retain.

Polyvinyl Acetals (Polyvinyl Aldehyde Reaction Products)

Polyvinyl acetate becomes polyvinyl acetal by a process in which the acetate is hydrolyzed to an alcohol, which is in turn partially replaced by an aldehyde. This may be acetaldehyde, formaldehyde, or butyraldehyde, resulting in polyvinyl acetal, polyvinyl formal, or polyvinyl butyral, respectively.

Another industrial method is to convert the chlorohydrin to ethylene oxide, a cyclic ether, by means of sodium hydroxide. Heating the oxide with water in the presence of an acid catalyst causes the formation of ethylene glycol.

$$\begin{matrix}CH_2Cl\\|\\CH_2OH\end{matrix} + NaOH \longrightarrow \begin{matrix}CH_2\\|\\O\\|\\CH_2\end{matrix} + NaCl + H_2O$$

$$\begin{matrix}CH_2\\|\\O\\|\\CH_2\end{matrix} + H_2O \xrightarrow[\text{acid catalyst}]{\Delta} \begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$$

In the preparation of alkyd resins, the polybasic acid and polyhydric alcohol are cooked in a reaction kettle with various modifying agents. Other synthetic resins may be added to improve certain properties; drying oils and natural resins or resin acids may be added for the production of coating materials; plasticizers and vegetable oils or fatty acids may be used to produce softer or more flexible products; solvents and diluents have various purposes in addition to that of forming a resin solution for casting cements or coatings; and water may be used in the production of water emulsions.

When the resin is obtained in the form of a water emulsion, it may be used, with the addition of pigments, as a water paint. The particles coalesce on drying to form a smooth waterproof coating.

The A-stage liquid resin, the resin solution, or the finely divided solid resin (the latter usually with the addition of solvents) may be used to produce cements and coating materials. Alkyd resins find use also as a printing-ink base, and an ingredient of lacquers, in conjunction with cellulose acetate or nitrate. Other types of coatings produced are varnishes and baking enamels.

A flexible type of alkyd resin of special composition, containing plasticizers, can be used for casting shapes and even for compression molding, especially for compression forming of sheets, etc. The finished articles may be machined and polished.

The resin drawn off from the reaction kettle may be prepared for a molding compound either by precipitation of the dissolved resin in a finely divided state or by grinding the solidified resin in a mill. To the resulting powder or granulation are added lubricants and any desired fillers or pigments. As the resin is thermosetting, compression molding is usually employed. The prepared molding composition is worked by rubber compounding methods, then molded in a press and placed in the curing oven.

Manufacture of Vinyl Ester Resins

Vinyl ester resins have as their raw materials coal, limestones, water, and acid. Coke and lime under high heat yield calcium carbide which, with water, yields acetylene.

$$2CaO + 5C \longrightarrow 2CaC_2 + CO_2$$

$$CaC_2 + 2H_2O \longrightarrow HC{\equiv}CH + Ca(OH)_2$$

The acetylene may then be used for the manufacture of vinyl acetate, vinyl chloride, vinyl aldehydes, or various vinyl copolymers.

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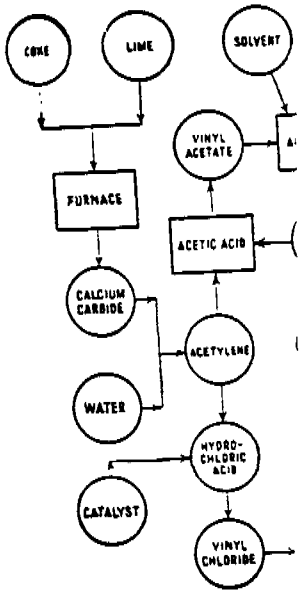

Fig. 13.10—

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In solution it is used

For vinyl acetate the acetylene is combined with acetic acid in the presence of a catalyst. When acetyl sulfuric acid is the catalyst, vinyl acetate is formed with little ethylidene diacetate, which latter interferes with the desired reaction when acetylene is passed into acetic acid, cutting down the yield of vinyl acetate.

$$CH{\equiv}CH + CH_3COOH \longrightarrow \underset{\text{vinyl acetate}}{CH_2{=}CH{-}OCOCH_3}$$

$$CH{\equiv}CH + 2CH_3COOH \longrightarrow CH_3CH(OCOCH_3)_2$$

Vinyl acetate, a liquid at room temperatures, polymerizes slowly to form a gel. At high temperatures this change occurs more rapidly and is further accelerated by the action of light and by various catalysts such as benzoyl peroxide, oxygen, silica, and bauxite. Perborates and percarbonates may be used but are less efficient catalysts. High temperatures yield a hard, brittle solid; lower temperatures, a tough resin of a higher degree of polymerization.

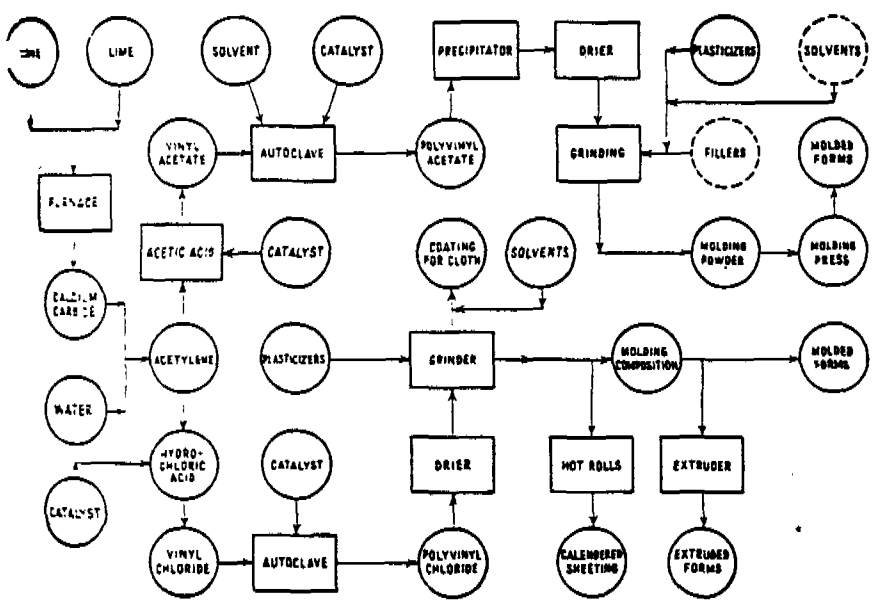


FIG. 13.10—Manufacture of vinyl ester resins. (Key on page 700.)

The action usually takes place in an autoclave, in the presence of a suitable solvent or diluent. By varying conditions, it is possible within fairly wide limits to produce polyvinyl acetate of predetermined characteristics. The resin is precipitated out, dried, ground and compounded as a molding powder, not commonly used for ordinary molding because of an objectionable tendency to cold flow. It is however used with various fillers in the manufacture of plastic floor tile, artificial leather, pressed wood composition, and surfacing for outdoor signs and panels.

In solution it is used as an adhesive and for coatings.

In the preparation of vinyl chloride acetylene is passed into a hydrochloric acid bath in the presence of catalysts such as ammonium chloride and cuprous chloride. As in the case of the preparation of vinyl acetate, ethylidene dichloride is produced, but its formation can be cut down by the use of silica gel or highly active carbon as a carrier for the catalyst. The reaction is carried on at a temperature of about 180° to 240° C. (356° to 464° F.).

The vinyl chloride produced is a gas at room temperature, liquefiable in a freezing mixture. It is polymerized in an autoclave to a tough linear polymer suitable for the production of plastics. The polymerization is accelerated by benzoyl peroxide or soluble lead salts. Varying the conditions of polymerization produces resins with a wide range of solubilities.

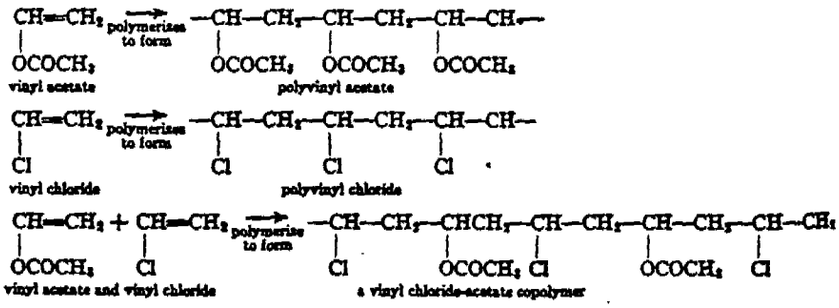
When plasticized, the resin (after compounding) is suitable for the production of molded products, transparent sheeting, and extruded forms. Some good plasticizers for vinyl chloride are tricresyl phosphate, dibutyl phthalate, dibutoxyethyl phthalate, and triglycol dihexoate.

The plasticized material is flexible and somewhat elastic and can be used for the production of flexible tubing and extruded wire insulation. Its excellent electrical insulating properties make it useful in the electrical field. Pigments may be added if desired, and fillers for molding compounds.

Vinyl chloride resin is incompatible with most other synthetic resins, and is inferior in many respects to the vinyl chloride-vinyl acetate copolymer.

Manufacture of Vinyl Chloride-Acetate Copolymer

If vinyl chloride and vinyl acetate are mixed and the mixture polymerized, a resinous product results which is different from and superior to polyvinyl chloride, polyvinyl acetate, or a mixture of the two.



This copolymer is formed by combining vinyl chloride and vinyl acetate in an autoclave in the presence of benzoyl peroxide. Its properties may be varied by changing: (1) the proportions of vinyl chloride to vinyl acetate in the reaction mixture; (2) the amount and nature of the solvents or plasticizers added; and (3) the conditions and extent of polymerization of the resin. Most commercial products are made with about 85 to 95% of vinyl chloride and usually are polymerized while mixed with a solvent. The polymer is usually precipitated with the aid of a nonsolvent such as water and is then dried with mild heat in a large continuous rotary

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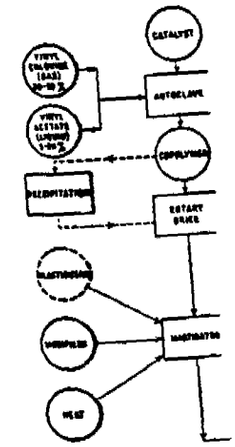

FIG. 13.

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mer. It is then worked in a masticator, and modifying substances are incorporated. The dried resin can then be fabricated either as a rigid stock or as an elastomer. In either case, a small amount of heat stabilizer such as lead stearate and/or basic lead carbonate is added prior to compounding. For rigid stocks, which are generally made from resin of not over 90% vinyl chloride content, no plasticizer is ordinarily used, the necessary modifiers being added and the material hot fluxed in an intensive mixer or roll mill and then formed into sheeting by calendering, or granulated, after cooling, to molding and extrusion material. For elastomeric materials, which are generally based on resin of higher than 90% vinyl chloride content, plasticizer such as dioctyl phthalate or dibutyl cellosolve phthalate is added, along with heat stabilizer and other modifiers, the material hot fluxed and then formed into granular material, tape, sheeting, film, coated on fabric, etc., as desired. Alternately the resin, with or without plasticizer, may be dissolved or suspended in suitable solvent or solvent-nonsolvent combination, and cast into films or coated on paper or fabric. Certain varieties of the resin may be dispersed cold in plasticizer to form compositions which although normally fluid, become, after short heat treatment, solid elastomeric masses. Such materials are known as Vinylite plastisols. In all these varieties colorants may be used as desired, the base resin being a transparent product.

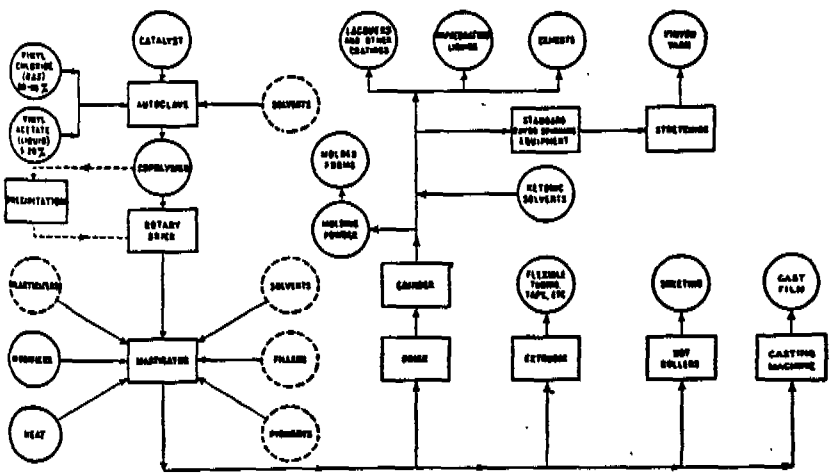


FIG. 13.11—Manufacturing of vinyl chloride-acetate copolymer.

In active practice, the same batch of resin is not used for applications, since resins of different molecular weight are suited to different applications. Usually copolymers of about 10,000 molecular weight are used for injection molding and about 12,500 molecular weight for compression molding. Extruded material and plasticized sheeting are usually made from material of an average molecular weight of about 21,000, whereas stiff sheet stock has a molecular weight of 15,000 to 16,000.

The dried and ground modified resin (a modification of about 9000 molecular weight), when dissolved in ketonic solvents and used as a coating material, makes a good chemical-resistant lacquer and has many uses. Sheets of material impreg-

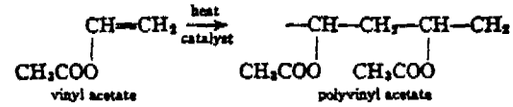
nated with the liquid may be pressed to a hard, durable, smooth, resistant finish. The dissolved copolymer is also useful as a cement.

One of the newest developments is the production of synthetic textile fiber from this copolymer. The material, of about 22,000 molecular weight, is dissolved in a ketonic solvent, usually acetone, and is spun to form fine filaments. Stretching these, while still more or less plastic, aligns the linear chain molecules lengthwise in the filaments, thus increasing tensile strength and elasticity. The resulting yarn may be woven into a variety of useful articles, the applications of which have not as yet been fully explored. Vinyon filter cloth is now in use.

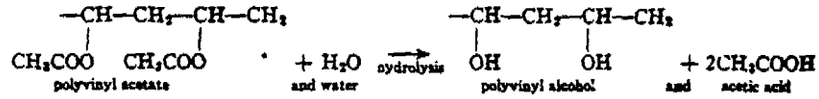
Manufacture of Polyvinyl-Aldehyde (Acetate) Plastics

Vinyl aldehyde resins are prepared by reacting a suitable aldehyde with polyvinyl alcohol, which is obtained by the hydrolysis of polyvinyl acetate.

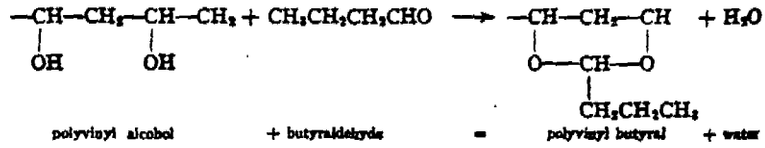
Vinyl acetate is first polymerized with the aid of heat and a catalyst such as benzoyl-peroxide.



The resulting polyvinyl acetate, dissolved in a liquid vehicle, is then caused to hydrolyze in the presence of an acid, or more usually, an alkaline catalyst. During hydrolysis the splitting off of the acetyl groups, leaving hydroxyl groups in their place, results in the formation of polyvinyl alcohol.



The polyvinyl alcohol is caused to react with an aldehyde, yielding as a condensation product a polyvinyl acetal compound. In the preparation of vinyl butyraldehyde, polyvinyl alcohol is reacted with butyraldehyde under the influence of heat and a suitable catalyst.



The process of hydrolysis and condensation may be carried on either separately or as one operation, but neither is carried entirely to completion. The commercial vinyl acetals contain small percentages of leftover polyvinyl alcohol and polyvinyl acetate, the presence of these substances apparently serving to improve the properties of the finished plastics, which properties also are affected by the amount of polyvinyl alcohol and polyvinyl acetate remaining (extent of the hydrolysis and condensation), by the type of aldehyde employed in the condensation and by the size of the molecules. The molecular size in turn is determined by the extent of

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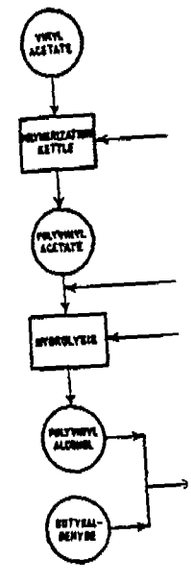

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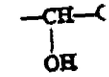

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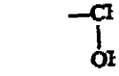


An example of a heat-convertible resin, one produced from a trihydric alcohol and a dibasic acid or by dihydric alcohols and acids with at least three carboxyl groups, would be the resin formed by glycerol and phthalic anhydride.

This resin is believed to have a branched chain structure somewhat like Fig. 18.25.

A different and interesting type of alkyd resin is the ethylene succinate type which forms long-chain molecules which lend themselves to the formation of flexible fibers. These are not heat-convertible except by the introduction of a small proportion of heat-convertible glycerol phthalate.

Addition Type Polymers

Vinyl Resin. The vinyl resins are derivatives of vinyl alcohol unknown in the free state and constitute one of the most important classes of addition polymers. The vinyl polymers and copolymers are linear chains in which the monomer units have joined to form useful high molecular weight polymers. The addition reactions are promoted by irradiation with ultraviolet light or by the use of small amounts of catalysts such as a peroxide, ozone, tetra ethyl lead, stannic chloride and others. Heat accelerates the respective reactions and autoclaves are required for the volatile monomers. The reactions may be carried out by bulk or emulsion polymerization—the latter leading to polymers of high molecular weights. The effects of oxygen on the various vinyl monomers are not fully understood. In certain instances oxygen acts as a positive catalyst—i.e., in the formation of polystyrene. Vinyl acetate polymerizes more slowly in the presence of oxygen when exposed to light. However, by heat alone the polymerization is slow unless a small amount of oxygen is present. The explanation may be found in the relatively large effects of small traces of impurities or by-products which as yet have not been carefully and fully investigated.

The polymerization of vinyl acetate, vinyl chloride, and their copolymer produces a structure as in

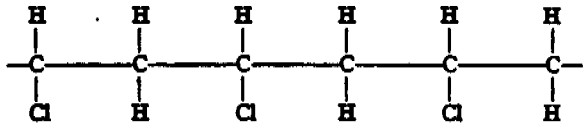


Fig. 18.26—Polyvinyl chloride.

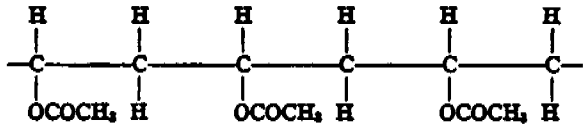


Fig. 18.27—Polyvinyl acetate.

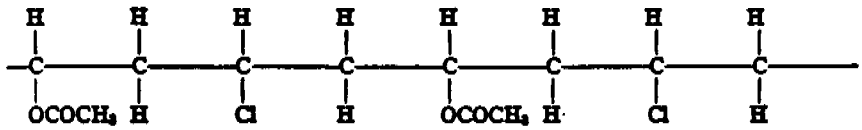


Fig. 18.28—Copolymer of vinyl chloride and vinyl acetate.

In contrast to the high water resistance of the chlorides the low molecular weight polymers of vinyl acetate are water soluble, and the entire range of acetate polymer does not possess the high water resistance of the vinyl chloride group.

The vinyl chloride resins are usually plasticized for commercial applications—selection of plasticizer being made on basis of original vinyl resin, intended application and method of fabrication.

Polyvinyl acetate is readily hydrolyzed by acid and alkalis. A complete hydrolysis gives polyvinyl alcohol—a useful commercial product for sizing formulations, for resists and hydrocarbon resistant tubing.

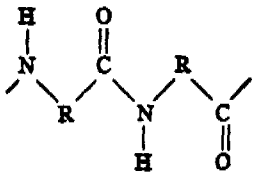


FIG. 18.29—Nylon structure. (See p. 1050.)

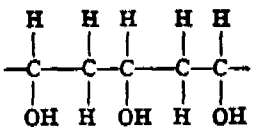


FIG. 18.30—Polyvinyl alcohol.

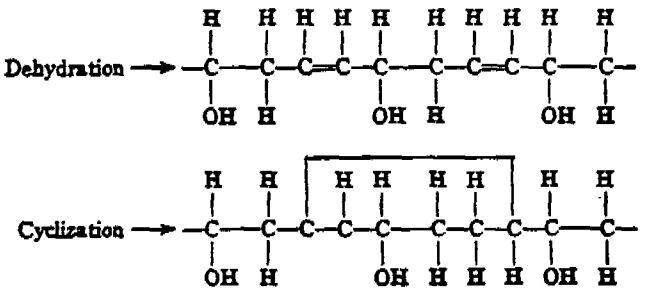


FIG. 18.31—Dehydration of polyvinyl alcohol.

Vinylidene-chloride resin, like the other vinyl polymers, is believed to have a long-chain linear structure consisting of monomeric units linked at the double bond as in Fig. 18.32. The similarity of this formula to that of polyvinyl chloride is obvious.

Vinylidene chloride can be made to polymerize with vinyl chloride to give a product like Fig. 18.33.

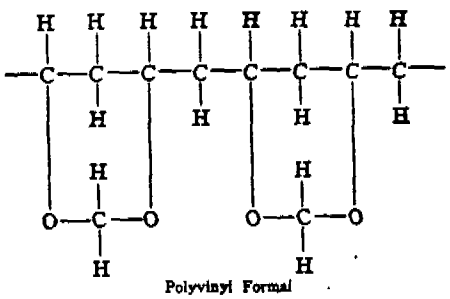
Acrylic resins include polymerized acrylic and methacrylic acids and their polymerized esters and salts. The esters, notably the methyl ester of methacrylic acid, are the most important.

Polymerized methyl methacrylate is believed to have somewhat the molecular configuration shown in Fig. 18.35.

Accordingly, ethyl acrylate would be represented by Fig. 18.36. Mixed esters (copolymers) may be prepared.

Polymerized acrylic and methacrylic acids are of course similarly formed as in Fig. 18.34. All these acrylic ester molecules have free end valences while they are still growing in length, but these are eventually stabilized.

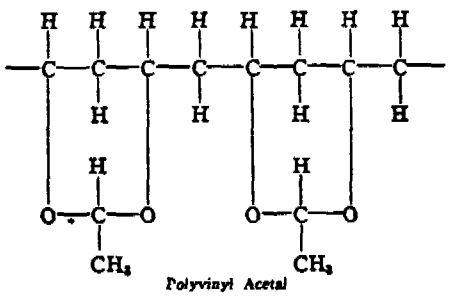
Polyvinyl acetal plastics. These are obtained from vinyl derivatives by hydrolysis and condensation with aldehydes.



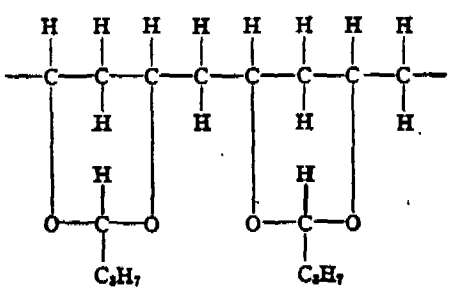
Polyvinyl Formal

The extent of hydrolysis is easily controlled to give products containing both acetyl and hydroxyl groups. Polymers containing free hydroxyl groups can be reacted with aldehydes to form acetals. It is obvious a large variety of materials can be prepared and that the properties of any specific product depend on the original ester selected, the extent of the hydrolysis, the aldehyde employed, and the extent of reaction between the alcoholic groups and the aldehyde.

Acetaldehyde and butyraldehyde likewise condense with vinyl polymer to give a similar structure. The structure of polyvinyl acetal and polyvinyl butyral may be represented as



Polyvinyl Acetal



Polyvinyl Butyral

Commercially these others.

Acetals are tough the corresponding a come widely used fo and acetate because ultraviolet light.

Vinylidene Chlor polymerize more ea polymers than viny oxygen polymerize temperatures above react to form acid catalysts for polym compounds, organo and inorganic acids various polymers a

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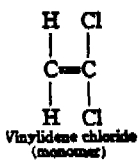

Vinylidene chloride (monomer)

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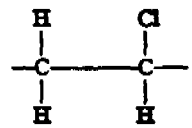


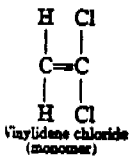
FIG.

Commercially these acetals are known as Formvar, Alvar Vinylite X, Butvar, and others.

Acetals are tougher, more resistant to water but less resistant to weathering than the corresponding acetates though the latter are harder. Polyvinyl butyral has become widely used for the interlayer in safety glass displacing entirely cellulose nitrate and acetate because of its superior toughness at low temperatures and resistance to ultraviolet light.

Vinylidene Chloride Polymer. In general 1.1 disubstituted ethylenes appear to polymerize more easily especially in the presence of oxygen and form less soluble polymers than vinyl compounds. The carefully purified 1.1 dichlorethylene free of oxygen polymerizes very slowly. Ordinarily the material polymerizes readily at temperatures above 0° C. due to the presence of traces of dissolved oxygen which react to form acid chlorides and peroxides capable of catalyzing the reaction. The catalysts for polymerization may be arranged into 5 groups—organic peroxygen compounds, organometallic compounds, organic carbonyl compounds, inorganic salts and inorganic acids. The straight line nature of these curves is characteristic of its various polymers and is evidence that the reaction is of zero order.

The vinylidene chloride polymers are not soluble in the monomer and separate as a precipitate in both mass and bulk polymerization, the character of the solid phase depending on the extent of the polymerization. The reaction is often controlled by the addition to the monomer of a solvent or an immiscible liquid and conducting the polymerization in solution, emulsion or other dispersed system.



Vinylidene chloride (monomer)

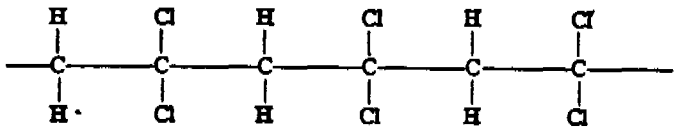


FIG. 18.32—Polyvinylidene chloride.

The copolymerization of vinylidene chloride and vinyl chloride has produced products which are somewhat easier to fabricate than the single vinylidene chloride copolymer without too significant sacrifice of the desirable properties of chemical and heat resistance.

The following formulae has been assigned to vinylidene chloride polymerized with vinyl chloride.

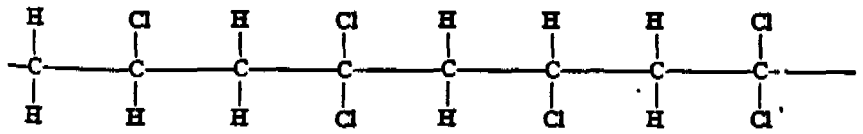


FIG. 18.33—Vinylidene chloride polymerized with vinyl chloride.

A piece weighing 3.8 gm., for a toy locomotive, cost $1.32 per 1000 pieces for material and machine operation at 1.5 cent per kw.-hr.

Power. Electrically powered and heated, no hydraulic pumps, valves, accumulators or pipe fittings needed. Only requirement—air supply 70–90 psi.

Output. 1 machine (60-sec. cycle) 1-cavity 1,000,000 pieces per 700 days
1 machine (60-sec. cycle) 4-cavity 1,000,000 pieces per 173 days
1 machine (60-sec. cycle) 19-cavity 1,000,000 pieces per 35 days

TABLE 22.3. COST STUDY OF AUTOMATIC MOLDING*

KEY

A — Completely Automatic Press (1-cavity mold)
B — Conventional Semi-Automatic Press (6-cavity mold)
C — Conventional Semi-Automatic Press (12-cavity mold)

	A	B	C
Delivery starts after (weeks)	2.0	3.5	4.0
Order filled in (weeks)	7.0	9.0	7.5
Mold costs (dollars)	450	1800	3000
Heat, power and labor costs (dollars)	15	125	80

* An order for 40,000 ash trays; production and cost comparison; various molding methods.

Workers' Welfare

In resin manufacturing plants, the problems of health maintenance are complex but not serious. Most plastics manufacturing plants are new, and due thought has been given to the workers' safety in setting them up.

Plastics are made from chemicals, and safety practices common to the chemical industry apply to those engaged in making resins or manufacturing products from them. Although the molder, unless he manufactures his own materials, has little direct contact with the raw chemicals used in resin manufacture, he nevertheless must give some thought to the health of his workers. Molding shops should be well ventilated to remove the dust and odors accompanying the use of molding powders. Some workers suffer from a form of dermatitis caused by phenol-formaldehyde molding compound due to a hypersensitivity to formaldehyde. Some workers are allergic to phenol itself.

In a study made by the U. S. Public Health Service ("Skin Hazards in American Industry," Part II, *Public Health Bulletin* 229, September, 1936, pp. 1–12), it was found that a large number of workers were sensitive to formaldehyde and others to phenol, cresol, or hexamethylenetetramine.

In order to determine to which of these substances the patient is sensitive, patch tests can be performed by a doctor with (1) a 4% solution of formaldehyde; (2) a 2% aqueous solution of phenol; and (3) dry powdered hexamethylenetetramine. The patches may remain on the normal skin for 24 hr. without causing a reaction. A sensitive individual will react to the patch of a substance to which he is sensitive.

To protect the workers against the irritants in phenol-formaldehyde resins, manufacturing processes should be totally enclosed. If this is not possible, hoods with

suction exhausts should be placed over open processes so that dust and fumes are drawn away from the worker and out of the room. The workrooms should be ventilated by intake and exhaust fans to remove dust and fumes. The floors, walls, ceilings, and machines should be washed down or vacuum cleaned at frequent intervals to keep them free from dust and irritating chemicals. Clean work clothes consisting of long sleeves, long-legged underclothes and long-sleeved coveralls fastened at the neck and wrists, and rubber gloves extending under the sleeves of the coveralls, should be provided. New workers who are hypersensitive to the resins but have only mild eruptions may be given protective ointments in addition to the protective clothing and may work for a period of three or four weeks in the hope that they will develop an immunity or become "hardened." If this does not occur, they should be removed from the job. If the patient's livelihood depends on his continuing at the job, an attempt may be made by a physician to de-sensitize him to the chemical to which he is sensitive. This should be done by beginning with minute doses administered subcutaneously and gradually increased. The results of each injection should be carefully watched so as to avoid severe constitutional reactions.

A textbook on the subject of toxicity of the various chemicals used in modern industry has been written by Alice Hamilton (*Industrial Toxicology*, Harper & Brothers, 1934). *Public Health Bulletins* 215 and 229, "Skin Hazards in American Industry, Parts I and II," describe industrial processes and their skin hazards in nineteen industries. These bulletins may be obtained by writing to the Surgeon General, U. S. Public Health Service, Washington, D. C.

When it is definitely determined that a worker is allergic to any of the ingredients of a molding compound, it is better to transfer him to some other work. In most cases of minor irritation, only cleanliness is necessary to ward off skin irritation. Some skin preparations can be applied which offer certain degrees of protection. The Milburn Company of Detroit markets one such preparation known as Ply. Such preparations usually consist of soap emulsions of stearic acid. The thin film of stearic acid protects the skin. The following formula has proved of merit in protecting workers' skin against some chemicals.

Stearic acid	18.0 parts
Amino glycol	1.5 parts
Glycerin	5.0 parts
Magnesium stearate	10.5 parts
Water	65.5 parts

The stearic acid should be melted. The amino glycol and glycerin should then be dissolved in water heated to the same temperature as the melted stearic acid. Mix thoroughly the two solutions. To this mixture add the magnesium stearate. The consistency of the mix may be controlled by the addition of further amounts of water.

One problem of protecting the worker in molding shops consists mainly of setting up protective devices around fast-moving presses, gears, and the like, and is approached in exactly the same manner as in a machine shop. When cold molding was more predominant, missing fingers were common identification of the molder's trade. Fortunately, this problem has been nearly eliminated with compression molding. With the automat
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ing. With the automatic injection molding machines, safety guards are incorporated at the outset and should be left on the machine.

Operations involving milling are dangerous unless adequate protection is afforded. The milling of plastics materials requires appreciable power, and there is ever-present danger that a careless operator may be caught accidentally while handling the material on the mill. Inasmuch as the equipment is unique to the rubber and plastics industries, the design of safety equipment for the mills is also unique to this class of machinery. The problem has three important phases.

The first of these is the design of power cutout and adequate braking in order to stop the equipment quickly and without damage. The second is a suitable arrangement of tripping devices located to permit almost involuntary operation by an operator in distress. The third is largely a question of an employer's responsibility to his operator to install and maintain the best available safety equipment.

The first rubber mills had no power cutout, no brakes, and no method of stopping, except the use of an obstruction thrown into the bite of the rolls. This has frequently been referred to as a "crowbar" brake. Although the method often would stop a mill, the operator did not always have within his reach a suitable implement to throw into the bite of the rolls. When such an implement was found the inevitable result was severe damage to the rolls or frame of the mill. After stoppage of the mill was accomplished, however, it was not certain that fracture of one of the rolls would permit rotation of the portion of the broken roll on the gear end. This was obviously an inadequate method of braking from several important points of view.

The first important advance was the introduction of a throw-out clutch on the high-speed drive shaft. Then, even after the clutch was disconnected, the rolls were carried through several revolutions by inertia. As mechanical drives from line shafts gave way to electric motors the mechanical throwout became unnecessary, but brakes were still lacking.

Today both mechanical and electrical brakes are available. Both classes operate on the high-speed drive shaft and utilize the mechanical advantage of the chain of reducing gears to obtain quick stopping action. The mechanical type of brake employs a weight-actuated lever as shown in Fig. 22.3 to apply the brake. Normally, the lever is in the elevated position, but when the release mechanism is operated, the power to the electric drive is cut off and the brake lever is released. The brake of Fig. 22.3 is electrically held by a solenoid and is applied by breaking the current through a solenoid. Mechanically held brakes are also used, and these employ a system of levers terminating in a hook on the brake lever to apply the brake simultaneously with the switching off of the power to the motor. The motor in either case cannot be started again without resetting the brake by hand. The electrically held brake has the advantage of remote control and is better suited to multiple-mill installations driven by a single motor. Further reference to Fig. 22.3 will show that a catch is provided to lock the brake as soon as it is once applied.

Mechanically actuated brakes, whether electrically or mechanically held, provide rapid and positive stoppage of mills without injury to their drives or rolls. They are simple and reliable in operation and low in first cost and are used in the majority of installations for these reasons.

Electric braking on mills and calenders is relatively new. The three major groups in the electrical class are dynamic braking, regenerative braking, and plugging.

Both dynamic and regenerative braking require that the mill drive be either a synchronous motor or a direct-current motor. This requirement often necessitates a compromise with the type of motor drive that might otherwise be chosen for the service. Dynamic braking is rapid in the early stages, but an intrinsic fault of the method is that its effectiveness drops off as the speed decreases. It involves a succession of changes in electrical connections by heavy contactors and the use of relays to give full field for effective braking. The equipment is expensive and requires specialized maintenance skill to assure reliable operation. Regenerative braking has the advantage of maintaining full braking power at all speeds and does not involve the opening and closing of heavy contacts. This method is applied chiefly on direct-current adjustable voltage calender drives, but it is high in first cost.

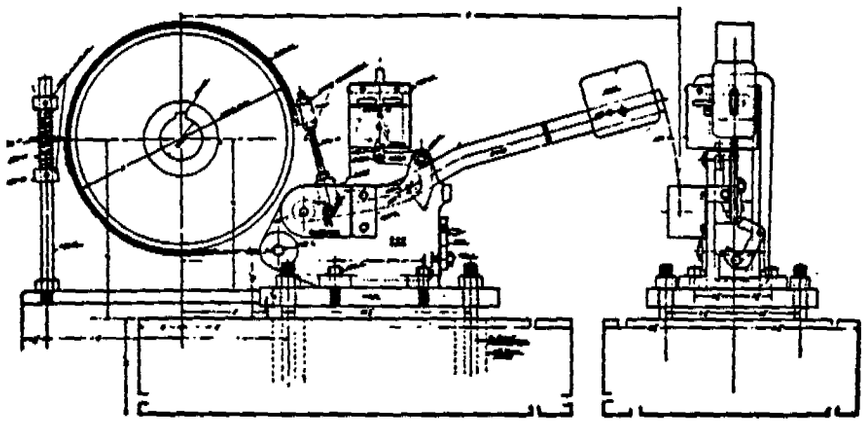

FIG. 22.3—Mechanical type of brake.

The third group, employing plugging, is applied to polyphase induction motor drives. This consists of changing the electrical connections to reverse the motor while running at full speed. It requires the use of control equipment to change the electrical connections, including relays to disconnect the motor as it approaches a dead stop. This method is not approved by some of the states for the machinery of the rubber and plastics industries.

The second phase of the safety problem, involving the proper arrangement of tripping mechanisms, has received a great deal of study. The first is a safety bar that is usually adjustable in height. This can be operated by the head or free arm of the operator and should be placed at about shoulder level to be readily accessible and most effective. The other arrangement is a safety cable at either side of the calender in such a position that it can be operated either by the free arm or by foot. In some cases other devices that can be operated by foot have been provided. It has also been proposed that mills be equipped with photoelectric cells and a beam of light passing from one side of the mill to the opposite side where it is focused on the photoelectric cell. Any opaque object that passes through the beam will actuate the brake mechanism and stop the mill. T
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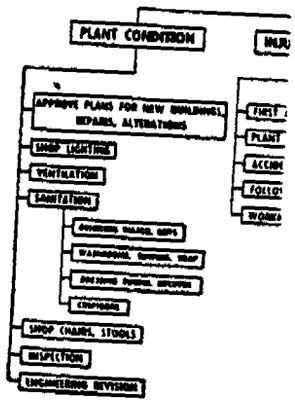

FIG. 22.4—Outline of activitie
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3. "Safety First and Efficie

nism and stop the mill. This form of tripping mechanism could be relied upon as definitely as any, but it has the disadvantage of being inconvenient while materials are being added to the mix on the mill or at times during the ordinary manipulation of the batch on the rolls.

The third phase of this problem is perhaps the most important one at the present time. It involves the obligation of employers to ensure a reasonable degree of safety to their operators in the milling and calendering of rubber and plastics. Unfortunately, it is still necessary that certain employers be forced to accept safety devices.

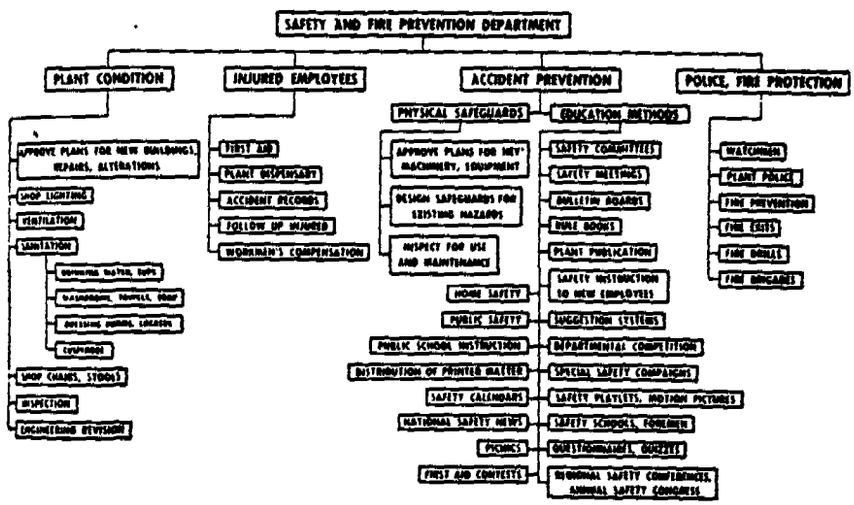

FIG. 22.4.—Outline of activities for a typical safety and fire prevention department. These duties are described in detail in Safe Practices Pamphlet No. 42 of the National Safety Council.

It is also unfortunate that safety devices are not always properly maintained in effectiveness. Rigid and periodic inspection of installed safety equipment should be the practice of every mill room. Much remains to be accomplished in the adoption of safety codes by the various states, although precedents have been established. Essential features of such codes are specifications governing the location of tripping bars and cables, and the statement of maximum roll travel for a given mill after the brake is applied. Various methods may be employed to measure roll travel. For example, an electric pencil operated by a mercury switch temporarily mounted on the trip bar may be used. In spite of the fact that the rubber industry is today one of the heavy industries, and in spite of the fact that the mixing of rubber is definitely hazardous, certain of the important states in the rubber industry today have no safety code. It is appropriate that this opportunity be taken to emphasize the importance of enforcing safety installations.

References. 1. "Safety Code for Rubber Mills and Calenders," Bulletin No. 447 of the United States Bureau of Labor Statistics, United States Government Printing Office, June, 1927.

2. "Tentative Safety Code for Mills and Calenders," State of New Jersey, Department of Labor, Bureau of Electrical Equipment, C. George Krueger, Deputy Commissioner, November 1, 1939.

3. "Safety First and Efficiency," by Joseph W. Thropp, *The India Rubber World.*

TABLE 22.4. DISABLING INJURIES, 1939, CHEMICAL INDUSTRY, BY INDUSTRIAL GROUPS*

Industrial Group	Number of Industrial units	Man-Hours Worked (thousands)	Average Number of Employees	Number of Disabling Injuries				Time Charges				Injury Rates	
				Death and Perm. Total	Perm. Partial	Temporary Total	Total	Death and Perm. Total	Perm. Partial	Temporary Total	Total	Frequency	Severity
All groups	417	305,535	144,378	40	172	2,073	2,285	240,000	106,005	39,090	385,095	7.48	1.26
Laboratories	13	4,202	2,062	0	0	3	3	0	0	16	16	0.71	0.003
Industrial Gases	8	4,303	2,109	1	1	5	7	6,000	60	101	6,161	1.63	1.43
Alcohol and Solvents Manufacturing	5	2,010	951	0	0	7	7	0	0	124	124	3.48	0.06
Plastics Manufacturing	16	13,485	6,704	0	15	36	51	0	4,459	647	5,106	3.78	0.38
Acid Manufacturing	40	19,739	9,623	4	16	56	76	24,000	10,250	1,701	35,951	3.85	1.82
Chlorine and Alkali Manufacturing	12	15,206	6,645	2	3	57	62	12,000	400	2,246	14,646	4.08	0.96
Carbon Products	13	9,397	4,629	1	12	35	48	6,000	6,497	1,013	13,510	5.11	1.44
Dye Manufacturing	7	11,602	5,752	1	7	56	64	6,000	3,268	1,268	10,536	5.52	0.91
Paint and Varnish Manufacturing	37	21,864	10,742	1	4	136	141	6,000	1,500	2,878	10,378	6.45	0.47
Pharmaceutical and Fine Chemical Manufacturing	29	43,631	15,977	3	13	377	393	18,000	9,728	5,655	33,383	9.01	0.77
Explosives Manufacturing	59	27,702	13,822	11	20	253	284	66,000	12,810	4,347	83,157	10.25	3.00
Soap Manufacturing	31	24,760	12,556	2	32	234	268	12,000	15,573	5,129	32,702	10.82	1.32
Coal Tar Distillers	17	1,155	558	1	0	16	17	6,000	0	224	6,224	14.72	5.39
Fertilizer Manufacturing	12	8,150	4,018	3	6	122	131	18,000	5,850	2,186	26,036	16.07	3.19
Salt Manufacturing	12	4,340	2,163	0	2	74	76	0	700	1,508	2,208	17.51	0.51
Vegetable Oil Manufacturing	30	7,609	3,850	0	9	131	140	0	8,315	2,473	10,788	18.40	1.42
Not Otherwise Classified	76	86,380	42,217	10	32	475	517	60,000	26,595	7,574	94,169	5.99	1.09

*Chemical & Metallurgical Engineering, October, 1940.

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As a whole, plastics enjoy a fairly low workers' injury rate, as may be seen by referring to Table 22.4, page 1212.

Most of the molding powder manufacturers maintain some sort of clinical service for their employees. A characteristic example of such an operation is followed by one producer of molding powder, who has a small infirmary in which employees may consult a doctor daily at a specified time. In addition every employee is required to have a thorough medical examination at the local clinic. At no cost to himself he is given a real "going over" including X rays of the chest. All new employees are checked and, if found to have respiratory trouble, are kept under surveillance. If the condition is aggravated by working with molding powders, they are transferred to other work or released.

Safety education should be encouraged in molding and resin plants. The following chart should be of interest in promoting workers' safety.