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PHENOLIC RESINS AND MOLDING MATERIALS

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PHENOLIC RESINS AND MOLDING MATERIALS

The term, phenolic resin, includes a broad variety of products being made by reacting a phenol with an aldehyde under various processing conditions. Such a reaction was first described by Baeyer in 1872. However, little attention was paid to the resinous reaction taking place between phenol and formaldehyde until the period 1890-1910. During this time, it seems that the principal effort of the investigators was to produce an artificial shellac. None of the products produced in these investigations was a commercial success as a shellac substitute. Neither were they successful as molding compositions because the resins were too brittle and porous.

Dr. Leo H. Baekeland studied the phenol formaldehyde condensation products from 1905-1909 and soon realized that they could not be handled in the same manner as the conventional resins of that period. He made two proposals to overcome the difficulty previously experienced in molding the phenolic resins. They were (1) the use of a filler to overcome the brittleness, and (2) the use of heat and pressure during molding. The application of pressure overcame the bubbling and porosity which earlier investigators had observed, and the temperature could be raised to the point where short molding time was obtained. Baekeland announced his discoveries in 1909.

Thus, the phenolic resins were the first commercial synthetic heat-hardenable plastics. They have been made and sold for almost fifty years. During this time, annual production has been consistently large and technological applications quite varied.

The resinoid is the prime ingredient in phenolic plastics. The fillers, such as woodflour, asbestos, fabric or paper, are used to accentuate certain properties. Some of these desired characteristics are better molding qualities, greater strength, and better heat resistance. Because of their dimensional

stability, electrical insulating qualities, chemical resistance, and economy, the phenolics are outstanding among the moldable plastics. Their unique combination of properties is responsible for their widespread use throughout all branches of industry.

The commercial phenols are phenol, cresol, xylenol, p-t-butyl-phenol, p-phenylphenol, bisphenol and resorcinol. The most important aldehydes are formaldehyde and furfural. Commerically, the most commonly used are phenol and formaldehyde, phenol and furfural, and resorcinol and formaldehyde.

PHENOL-FORMALDEHYDE

Two general types of reactions are employed in the manufacture of phenol-formaldehyde resins, involving different ratios of formaldehyde to phenol with acid and alkaline catalysts, respectively. In either case, initial reactions of formaldehyde with phenol yield phenol alcohols. These aromatic alcohols then react with additional phenol and aldehyde to make extended and cross-linked resinous chains. Through control of purity and proportion of each reactant, reaction time, and temperature, resins of many diverse properties may thus be obtained.

If the reactants involve a ratio of at least one part of formaldehyde to one part of phenol, generally with an alkaline catalyst, the final product is referred to as a one-step resin. The initial phenol alcohols formed contain one or more methylol groups. These phenol alcohols are known as resols or A-stage resins, and are fusible and soluble in solvents and alkalies. One product of this intermediate A-stage is known as saligenin, which is available as a purified chemical. Through further reaction of the methylol groups, chaining and then cross-linking occurs. Thus, resols can be cured, on heating, to infusible insoluble products. As condensation proceeds beyond the A-stage, the resins enter the B-stage and are called resitols. Molecular weights of the B-stage resins are

of such a size that the resins are no longer readily soluble in alkalies, although they are still soluble, or partially soluble, in organic solvents such as acetone or alcohol. Cross linkage has not proceeded very far, and the resins are softened by heat, although hard and brittle when cooled. Resites represent the commercial stage of polymerization, with a large amount of cross linkage. Resites, or C-stage resins, are relatively insoluble and infusible.

If a ratio of less than one part of formaldehyde to one part of phenol is used, generally with an acid catalyst, the resultant resin is a novolak and is permanently fusible. If desirable, novolaks can be converted, with additional formaldehyde, to insoluble, infusible products. Hexamethylenetetramine is usually added to the pulverized novolak for this purpose because, under heat and pressure, it yields methylene and ammonia. With ammonia serving as a catalyst, the methylene completes the reaction, forming a resin referred to as two-step, which is capable of producing practically infusible and insoluble plastics.

Acid catalysis, typical of the conventional two-step resins, produce a phenolic resin of relatively slow cure. However, through the use of selective catalysts , it is possible to control the structure of molecular formations to produce resins of faster cure. By using oxides of zinc, aluminum, or magnesium as a catalyst instead of the usual acid, chaining takes place largely in the ortho positions on the benzene ring, thus leaving open the para positions for cross-linking and giving a commercial phenolic resin capable of rapid cure. Resins based on selective catalysts, but with intermediate rates of cure, are possible to produce by careful control of reaction conditions. These include catalysts, temperature, pH, ratio of reactants and reaction time. The states of resin formation are not clearly defined but pass gradually one into another. After the desired degree and type of condensation has been achieved, dehydration and purification is carried out until the desired viscosity is reached, and the liquid

resin is cooled. For varnishes and similar solutions, a solvent is added after substantially complete dehydration of the hot reaction mixture, and the product is cooled. Blending and filtering precede packing. Lump and powdered forms are produced by running the resin, after concentration and dehydration is completed, onto cooling floors or pans. The cooled resin is either broken into lumps and shipped as such, or ground to powder for further processing.

PHENOL-FURFURAL

Formaldehyde is the aldehyde used in greatest quantity by the phenolic resin industry; furfural is the most prominent of the aldehydes used for modifying purposes. Furfural as currently used by phenolic resin manufacturers contributes special and useful flow properties to the phenolic resins of commerce.

It is primarily used in reaction with synthetic phenol to prepare lump resins which in turn are ground and blended with fast-curing formaldehyde-phenol powdered resin in suitable ratios. Another obvious and practiced method is to react mixtures of furfural and formaldehyde with phenol in the reaction kettle itself. In either case the blends thus produced are either compounded with fillers in the case of molding powders, or become phenolic resins of commerce as binders for resinoid abrasive wheels, brake linings, adhesives, laminating varnishes, and the like.

In many uses of thermosetting phenolic resins, the ratio of the rate of flow under the application of heat, or heat and pressure to the time of cure, is the governing factor in the usefulness of a resin. This relation of the physical property of flow to the time required to convert the product to the infusible stage is recognized as being especially important in molding applications. The optimum balance of flow and rate of cure results in fast cure with the maximum to be had in strength and appearance of the molded piece.

In general and assuming the use of synthetic phenol as the phenol body, the lower the molecular weight of the aldehyde the shorter the flow period, due to increased cross-linking rate. In the case of formaldehyde the flow interval is very short; i.e., gelation is reached rapidly and complete cure follows almost immediately. In many phenolic resin uses, this is desirable, but for any important number of uses the flow interval of formaldehyde reaction products is too short. In the case of furfural, the flow interval is long due to a slow rate of reaction. Hence, the phenolic resin industry employs combinations of furfural and formaldehyde in numerous instances, thereby providing a complete spectrum of flow-cure properties. Technically, the phenol-furfural combination acts as a type of "inhibiting agent" that decreases the rate of reaction of the unreacted phenol and formaldehyde. The terms of "furfural-phenol" or "formaldehyde-phenol" are therefore coming less useful in being able to describe accurately the contents of most commercial phenolic resins.

Furfural as supplied commercially is essentially anhydrous and therefore offers an advantage in shipment and storage as well as in the manufacturing operation. Kettle capacity is enhanced since there is less water to be removed during the reaction period than with the use of formalin.

The single largest application of furfural in the phenolic resin industry is in the production of molding compounds. Five years ago the present giant-sized phenolic moldings were unheard of. Since that time phenolic molding powder manufacturers pioneered the development of long-flow compounds, and in cooperation with press builders and molders, made possible the deep-draw molding of a large TV console cabinet and other large and complex moldings.

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RESORCINOL-FORMALDEHYDE

Resorcinol has a higher rate of reactivity than phenol under some conditions. The order of reactivity of resorcinol with formaldehyde is such

that no catalysts are necessary to induce reaction, and reaction will take place under alkaline or acid conditions. By reacting one mol of resorcinol with substantially less than one mol of formaldehyde, novolak resins are obtained which are permanently fusible and soluble in water, ketones, alcohols, esters, and similar organic solvents. These resins can be repeatedly heated with no substantial change in properties. By dissolving in a solvent medium, usually water and alcohol, and adding a catalyst in an amount sufficient to bring the $_{p}H$ of the solution to approximately 7, an adhesive base is formed which can be set in the presence of a hardening agent, generally formalin or paraformaldehyde. In a similar manner, copolymer phenol-resorcinol-formaldehyde adhesives can be prepared which set at a $_{p}H$ of about 8 and show about the same reactivity as shown by resorcinol adhesives.

Variation in properties of resorcinol resins are found to be a function of $_{p}H$ as well as of the formaldehyde-resorcinol ratio. Some resins are capable of reaction at room temperature, and many commercial adhesives are formulated to set at 75 to 90° F. within controlled time periods of several minutes to several hours. Reaction in the presence of heat can be made almost as flash cure rates. Such rapid-hardening blends, however, may give aging difficulties (high rate of color change to light exposure) at room temperatures.

Selected resorcinol adhesive mixtures are characterized by reasonable stability. However, loss of solvents due to opened containers may alter the formulation. Use of fillers, such as walnut shell flour and the like, has been found effective in increasing the strength and stability of glue lines. In proper proportions, these fillers give optimum performance in toughness and in resistance to cracking,

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Resorcinol resins can be used quite generally where phenolics are used. The low temperature cure is particularly helpful in the fabrication of heavy

structures with thick sections where slow heat retards the cure of normal phenolics, or in gluing odd-shaped pieces that cannot be handled well between the flat platens of a hot press. Because of their high affinity for wood, the most important use of these resin adhesives has been in wood gluing, particularly for marine plywoods. Less well-known applications are in various bonding operations on laminated and molded phenolics, nylon, and other plastic materials.

Industrial Resins

The term "industrial resins" originates from the large number of industries that find that phenolic resins are a necessary part of their product formulation. The ultimate consumer rarely realizes that these products contain phenolic resin, and the products are not usually regarded by the public as plastics.

The industries consuming large quantities of phenolic industrial resins include those that manufacture exterior grade plywood, laminates, heat and sound insulation, grinding wheels, abrasive paper, foundry molds, rubber goods, wood waste products, insulating varnishes, castings, and a host of other end products in which the use of phenolic resins makes a better article possible.

Industrial phenolic resins are generally tailor-made for a specific field of use and frequently for an individual user. The versatility of the phenolic system of resins is brought out in the industrial applications. No other resin system fits so many diversified fields.

The properties which make phenolic resin so popular in the industrial field include heat, chemical, water, and corrosion resistance, electrical insulating qualities, and bonding properties for a wide variety of materials.

Molding Materials

Granular and macerated molding materials - Both one-step or two-step

resins or their many variations are employed for these materials, the type selected depending on properties desired. The heat-reactive resins are used as such by condensing further and processing with dyes, lubricants, and/or plasticizers until the desired molding properties are achieved, or are compounded with fillers for the purpose of further modification of the properties. The latter include compounds that incorporate either organic or inorganic fillers in ground or in macerated form. Woodflour, cotton flock, asbestos, and similar granulated products; or macerated natural or synthetic fabric, fibers, or films; or paper are fillers frequently employed. Fibrous glass, chopped glass cloth, and the new synthetic fibers have recently been introduced as fillers, presenting interesting new properties. Sometimes the molding compounds are too bulky due to the incorporated filler and are further processed to produce a product that is in a pellet or nodular form. This form facilitates handling and preforming during the molding process.

The various phenolic molding compounds are often designated by the properties they impart to molded products, and are commonly known as general purpose, shock-resistant, heat-resistant, and special purpose phenolics. When fully cured, phenolic molding compounds are relatively inert. With the exception of special grades, they are measuredly decomposed by strong caustic solutions. Molded pieces are hard, rigid, durable, and difficult to ignite or slow burning. Because the usual phenolic materials show a marked tendency to discolor when exposed to light; dark colors are recommended. Indoor aging characteristics are good. In general, curing temperatures range from 275 to 350° Fahrenheit. Unless special grades of materials and special techniques are used, pressure is required for the cure. Compression, transfer, or plunger techniques, which increase the flow and alignment of plastics, can be employed. Large pieces can be successfully molded and show good tolerance for inserts. The range of end products which phenolic molding materials provide is almost unlimited.

Phenolic resin boards and blanks - Phenolic resin-pulp boards are produced on a wet cylinder machine, usually in standard size sheets, 48 by 66 in., and thicknesses ranging from 0.031 to 0.045 inch. From these boards the manufacturer supplies sheets, strips, rectangles, special shapes, and diced material. Products are characterized by low bulk factor and relatively high mechanical strength, dimensional stability, and moisture resistance. Properties can be somewhat tailored by variations in the processing. The material can be handled in molds for general purpose phenolics. It can be used either for producing finished pieces or in conjunction with standard phenolics to provide reinforcement. In many cases the proper use of blanks with other molding materials will produce a piece having a combination of mechanical and dielectric strength, and good color not obtainable in the boards alone. Resin boards and blanks are suitable for the production of many industrial and household items.

Phenolic pulp products - By the use of pulp resin preforms, articles may be made up of layers in which the body or core contains a high percentage of fiber and a low amount of resin, while the surface layers are richer in resin than fiber. When cured, the several layers are firmly bonded by the fluxed and hardened resin into a single piece, whose surfaces have high resistance to wear or fluids which may come into contact with them. The body layer, due to its high fiber content, gives the article its high strength. A recent development, covering the use of decoratings or inserts on the surface of serving trays or other flat pieces, finds the shaped preform particularly advantageous, as it offers a flat surface on which these items may be easily and accurately placed. For complex shaped articles and articles of varying sectional thickness, for which molded-to-shape preforms are not adapted, a special pulp resin blank is used. This blank is also vacuum felted from an aqueous pulp resin mixture to the shape best suited for obtaining uniformity of pulp and resin distribution in the finished product, when compression molded in the conventional manner. The high

strength of the finished article results from its fiber structure being unchanged, except for compacting, from its condition in the original preform.

Rubber-phenolic compounds - Within the past few years, use of phenolic resins with synthetic rubbers, such as GR-A, GR-S, and "Neoprene," has made possible improved molding compounds which process readily, cure faster than rubber, and produce finished articles of special properties. The resin in moderate quantities can act as a reinforcing agent for the rubbers, imparting hardness, or the rubber can be utilized as a plasticizer for the resin, giving a product which is softer and tougher than that which is otherwise obtainable with phenolic resins.

The rubber-phenolics have interesting properties which permit them to compete with metals, wood, ceramics, thermoset laminates, and straight phenolic molding materials. They generally mold well in molds that have been constructed for general-purpose phenolic materials. Mold shrink allowance is sometimes a more intangible factor than for other phenolics, but a full scale of shrink allowance has been established for some of the blends.

An inherent characteristic of rubber-phenolics is the relative resiliency of the material on release from the mold. Thus, the design and location of knockout pins have to be carefully considered. In parts requiring great accuracy, shrink fixtures for slow cooling are frequently used. The best molding temperature is reported to be between 340 and 350° Fahrenheit. Cycles may be up to 20% longer than for standard phenolic materials, and minimum pressures should be used commensurate with the proper density of the molded part.

The rubber-phenolic molding compounds are ideally suited for transfer or plunger molding, because they are fundamentally soft and have a long duration of flow.

Molded parts containing rubber do not need as much reinforcement from

the standpoint of ribbing or fluting, or excess radii at corners, or thicker sections, as do standard phenolics.

Phenolic resin-asbestos composition - A phenolic resin-asbestos composition ("Haveg", Haveg Corp.) has been developed which makes possible the economical production of large, complex pieces of equipment through simplified molding techniques. This material is available from the manufacturer only in the form of finished equipment--factory molded to the desired shape. The molding process consists of packing a putty-like composition into a simple mold in which the resin is cured under controlled temperature conditions without using a hydraulic press. Because of the simplicity of the mold construction, this procedure is used to produce small quantity runs or even individual pices without the introduction of prohibitive mold amortization charges into the final price.

The asbestos filler used is acid digested and the baked product is, therefore, resistant to almost all non-oxidizing acids, salts, the weaker bases, and many solvents. Graphite is substituted for the acid-washed asbestos in equipment intended for hydrofluoric acid or acid solutions of its salts. These compositions are characterized by strength, toughness, and resistance to thermal shock, and can withstand sustained temperatures of 300° Fahrenheit. Large molded pieces which are subjected to considerable hydrostatic heads or gas pressures are provided with external support, which usually consist of steel ribs or wood staves with steel hoops. It is possible to make field alterations or repairs with cold setting cements which, when hard, have comparable chemical resistance to the baked phenolic material.

In addition to the basic types discussed, phenolics may be classified according to their intended use in commercial and industrial applications.

General-purpose phenolic materials are distinguished by their all-round

serviceability. This class of products consists generally of cellulose-filled materials and are capable of being molded under a wide variety of conditions, producing parts of clean lustrous finish. Easiest to handle, and frequently the most economical to use, they possess a broad range of molded properties that will meet the requirements of a majority of applications. Typical applications for these materials include wire devices, components for household appliances, brush handles and automobile parts.

General-purpose phenolics with improved water resistance are used for closure materials such as bottle caps and jar covers. Certain general-purpose phenolics are designed to impart prime quality in appearance. Camera cases, radio cabinets, molded drawers, and telephone parts exemplify this particular resin.

General-purpose materials with improved impact strength possess from 1.3 to 2.0 times greater Izod impact strength than other general-purpose resins. For this reason, they are used in instrument casings, meter housings, and washing machine agitators.

Special high impact-resistant phenolic materials offer up to sixteen times the Izod impact strength of the general-purpose phenolics. In addition, some of these materials have improved moisture resistance under longer periods of immersion, exposure to high humidities and at high temperatures of immersion. These paper, fiber, pulp, fabric and cord-filled materials possess impact strengths in the range of 0.60 to 8.0 ft./lb. per inch of notch.

Very often the use of molded parts requires a shock resistance greater than that obtained with general-purpose. For this reason, high impact resistant phenolic came into being. The user of molded parts should bear in mind that the greater the shock resistance of the material, the more difficult it will be to

mold. This is because of the bulk factor encountered in the type of filler employed. Consequently, the purpose of having a range of shock-resistant materials available, is to provide intermediate impact strength which is adequate for a given use without unnecessary sacrifice of molding and performing qualities. Uses of shock-resistant materials range from telephone handsets and tool housings to heavy duty flashlight cases and oil-well drilling equipment.

Heat-resistant phenolic is another important class. While being the most dimensionally stable of all phenolics, this material provides a maximum degree of heat resistance in conjunction with other necessary products.

Heat-resistant phenolics are somewhat more difficult to process in the tabletting and molding operations than the cellulose-filled materials, and parts molded from them are less easily machined. This is caused by the presence of a mineral filler.

These materials are employed when higher heat resistance and better water resistance are desired. Furthermore, they have a lower coefficient of heat expansion and lower shrinkage in the molding operation.

A number of these materials has been developed, each especially suited to a particular type of service. Applications include molded commutators, heater connectors, outdoor insulation, handles of toasters and cooking utensils and other uses where the special property of better heat resistance is required.

Low-loss electrical phenolics are another example of the application of phenolics in specialized uses. This material is recommended for use where low power factor, low loss factor, high resistivity, dimensional stability, and low water absorption are desired. Capacitor casings and frames, condensers, coil forms, automobile and aircraft distributors and resistors typify its use in the electrical field.

There are many so-called "special phenolics." These include diverse materials used in applications requiring particular properties or particular combinations of properties. One example would be phenolics with improved chemical resistance. This type would be utilized in vaporizers, milking equipment, automatic washing parts, bottle caps and other applications where resistance to water, acids, alkalies, oils and greases are likely to be encountered.

Low frictional phenolics are used in products requiring a low coefficient of friction, such as heavy-duty bearings and caster wheels. There is even a special phenolic formulated for x-ray tube housings and component parts of x-ray equipment. This material is employed to prevent the escape of radiation.