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PROCESS FOR THE PREPARATION OF HARDENED SYNTHETIC RESINOUS PRODUCTS

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This invention relates to processes for the production of hardened resin products from mixtures of soluble phenolic resins and amide-formaldehyde resins.

When resinous products are prepared in accordance with prior art practices from urea or other amides and aldehydes, the intermediate liquid condensation products, whether such products are used to form molded resins or to form resin films, pass into the gel or solid state very rapidly through the action of acid catalysts and are hardened during a thorough heat treatment forming final products subject to internal stresses and strains, which are brittle, are subject to cracking and possess poor water, alkali and alcohol stability. The colorless urea resins formed harden very rapidly, adhere poorly, tear very easily, have poor mechanical strength and are very unstable toward chemical reagents. The good properties of such products include their power of dissolving dye and their color stability in the presence of light and heat.

As compared with urea resins, the phenol resins in thin films, including both the intermediate products and the acid hardened final products, are somewhat better with reference to hardening speed, adhesive quality, stability and mechanical strength. The phenol films have the disadvantageous properties, however, of possessing a porous surface and of having a tendency to yellow when exposed to light, and sometimes even when kept in the dark.

The object of the present invention is to produce a superior resin which does not have the disadvantageous properties possessed by these individual resins or resin classes. In accordance with the present invention, products are produced which overcome entirely or strongly suppress the objectionable qualities of the above mentioned resins.

The process of the present invention in its broader aspects involves the preparation of hardened resin products by mixing phenol resins of the resol or soluble type with amide-formaldehyde condensation products in suitable proportions and reacting and hardening the resulting mixed resin through the action of a known hardening catalyst, which may be incorporated in the mixture in any one of a number of suitable ways, as hereinafter explained. The products obtained by my new procedure have been found to a surprising degree not to possess the disadvantageous properties of the single resin components and to have properties which are superior in several respects to the hardened products obtained from the individual resins. One advantage over the phenol resin lies in the greater rapidity with which the hardening of the resin mixture occurs due to the action of the hardening catalyst.

The final hardened resinous products of the present invention are particularly outstanding because of their high degree of elasticity and considerably improved water stability when compared with the final resinous products obtainable from the individual resin components. A second outstanding advantage resides in the greater adhesive property of the mixed resin. These superior properties arise through the catalytic hardening of the mixed condensation products obtained by the simultaneous action of the phenol resin and the urea resin in forming a new resinous substance having new and different properties.

No novelty is claimed in the preparation of mixtures of phenol resins with urea resins per se, for such mixtures have been described in the prior art. The novelty of the instant invention lies particularly in processes for the production of superior final condensation products composed of mixtures of such resins in proper proportions and wherein the final condensation, polymerization and hardening is effected solely or primarily through the action of hardening catalysts.

The mixing of the resins may be accomplished in several ways. The raw materials suitable for the production of the individual resins may all be put into a single mixture and the condensation effected simultaneously, or the non-aldehyde component of the one resin type may be added to the more or less preliminarily formed resin of the other type, after which the condensation of the one resin is effected while in admixture with the other. Alternatively, both of the intermediate or soluble resins may be completely formed before mixing and afterwards fused together and subjected to a hardening treatment with or without a filler.

In accordance with prior practices, mixtures of such resins have been converted into the final insoluble, infusible products through the action of a heat hardening treatment. The resulting products, however, did not possess properties of outstanding superiority over those of the individual resinous components. In contrast to these prior results, the instant processes wherein the mixed resins are hardened by the action of catalytic agents at ordinary temperatures, lead to the production of products which possess surprisingly superior properties.

For the preparation of the new resin masses of the present invention, soluble phenol resins, or

those of the resol type, are in general operable with varying degrees of success. In preparing the resins, the various types of phenolic compounds described in the prior art may be used, examples of such being phenol itself, cresol, polyvalent phenols and polynuclear phenols. The phenolic resin component may be prepared from these phenolic compounds through the use of any of the reactants of the prior art, including formaldehyde and, as well, other carbonyl compounds.

The amide-formaldehyde resin component of the mixed resin of the present invention is preferably prepared through the condensation of urea and formaldehyde. The invention contemplates the use of any fusible reaction product of urea and formaldehyde, whether it result from acid, neutral or alkaline condensation, or from a condensation involving any combination of such conditions, such as reacting at first under neutral or alkaline conditions and then under acid conditions, or from the use of such conditions in reverse order. At the time of the mixing operation in accordance with the present invention, the urea condensation product need not be in the resinous state, for it may be in the crystalline state, as when certain methylol urea compounds are employed, such as dimethylol urea or mixtures of dimethylol urea with monomethylol urea. Instead of urea, other urea compounds may be employed. The urea may be wholly or partially substituted by thiourea or other amine or amide compounds, such as aniline or dicyandiamide.

For use in the preparation of the mixed resins of the present invention, those urea resins are particularly suitable which have been partially or wholly dehydrated by drying or evaporation with the aid of a vacuum, or whose water content is distilled off with the aid of an alcohol or other organic solvent added thereto. In accordance with another embodiment, which leads to very good results, the urea resin component is one which has been subjected to a preliminary condensation treatment under slightly acid, neutral or alkaline conditions and thereafter further condensed in acid solution in the presence of alcohols or other hydroxyl group-containing materials, and preferably finally freed wholly or in part of the alcoholic solvent by evaporation.

In the production of the mixtures of the soluble phenol resin and soluble urea resin, the following procedures have been found to lead to good results. The urea and formaldehyde are first reacted to produce dimethylol urea and this reaction product is then mixed with the phenolic resin component which preferably has theretofore been neutralized with conventional agents, the resulting mixture next being heated and stirred in order to cause the resins to combine with each other to form a homogeneous mass. In accordance with a second method, both resinous components are formed separately and while in the liquid state are agitated together by means of a mechanical mixing apparatus at normal temperatures in order to bring about the desired homogeneous mixture. In accordance with a third method, one of the resins is dissolved in a solvent, for example, in ethyl alcohol or other alcohol, and this solution is then mixed with the other resin by stirring. In accordance with a fourth process, both resins are dissolved in suitable solvents, and the resulting solutions mixed together, and if so desired heated either with refluxing of the solvent or evaporating the same from the mass. The proportion of the resins used in producing the mixed resins may vary within wide limits, depending upon the nature of the particular resins used and the properties desired in the final product. Good results for many purposes are obtained when the phenol resin is used in an equal or greater proportion, but in any event substantial proportions of the phenol resin must be used.

The resin mixtures obtained by any of the foregoing procedures are then treated in accordance with a further step of the process of the present invention with a hardening catalyst which may be either alkaline or acid in character. The preferred catalysts are acids themselves or materials which split off acids, satisfactory examples of such substances being hydrochloric acid, sulfuric acid, phosphoric acids, hydroxyl amine chlorhydrate and the like. In accordance with a preferred embodiment of the invention, the catalyst is introduced into the resinous mixture while the former is in a dissolved state. This procedure not only effects a more uniform distribution of the catalyst throughout the mass, but enables one to introduce the exact proper quantity of the catalyst.

The resin mixtures containing hardening catalysts as described above may be used in many ways. Alcoholic or other solutions of said resin mixtures may be used as such or in combination with fillers, with dyes or with softening agents for the coating of many materials, such, for example, as wood, glass, metals and prepared compositions of various kinds, such as foils, threads, wires, woven materials, felted materials and the like. Furthermore, such resin products may be used as, or in the production of, cements, adhesives and packing materials. In combination with various fillers they may be used as molding resins or as plastic or cast materials, in which uses the acid hardening may be assisted by heat.

In the following illustrative examples all parts are given by weight.

Example 1

Phenol and formaldehyde are mixed in the molecular proportion of 1:1.5 and the mixture is condensed in the presence of sodium hydroxide for several hours at a temperature of from 60° to 70° C. After neutralization of the sodium hydroxide the water is distilled with the aid of a vacuum at a temperature of about 60° C. The resulting product is a viscous light resin. Then 20 parts of dimethylol urea are added to 200 parts of the phenol resin obtained. The resulting mixture is first heated to 100° C. to melt the dimethylol urea and is then stirred for 15 minutes, after which it is maintained at a temperature of 80° to 85° for a period of from 1.5 to 2 hours. The resulting mixture is then discharged into another vessel wherein it is immediately dissolved in an equal weight of ethyl alcohol. Then 100 parts of this solution is mixed with 5 parts of orthophosphoric acid in alcoholic solution. In this manner a coating composition in laquer form is obtained suitable for the coating of iron or wood and may be applied by brushing, spraying or dipping. After from 1.5 to 2 hours the applied coating forms a clear film which is no longer sticky, the film becoming relatively hard after from 3 to 4 hours.

Example 2

600 parts of urea and 380 parts of thiourea are mixed with 3,000 parts of a 30% formaldehyde solution and condensed under mild alkaline conditions at a temperature of from 30° to 40° C. While the condensation reaction is proceeding or

after the same has advanced slightly, the water is evaporated off. Then 250 parts of this urea-thiourea-formaldehyde condensation product is introduced into 300 parts of warmed ethyl alcohol containing 10 parts of urea nitrate, and heated to boiling for about one-quarter of an hour for the purpose of forming a homogeneous solution. After neutralization of the solution it is filtered and the alcohol distilled off with the aid of a vacuum. Then 100 parts of the acid hardened phenol resin, prepared in accordance with the procedure set out in Example 1, is mixed with 60 parts of the urea resin as above described and with 10 parts of glycerine as a softening agent. Finally, 10 parts of an 18% alcoholic hydrochloric acid solution is added and the resulting resin mass is poured into lead molds wherein it rapidly hardens to form a cast resin of the desired shape.

Example 3

Dihydroxy diphenyl dimethyl methane is mixed with formaldehyde in the molar ratio of 1:3 and is condensed in alkaline solution at normal or room temperatures. When a soft resin is obtained it is neutralized by the addition of an acid, the resulting mass then being washed and finally dehydrated at a mild temperature under a vacuum. 60 parts of urea and 360 parts of a 30% formaldehyde solution are brought to a pH value of 4.6 by the addition of a molar solution of sodium hydroxide. After boiling the mixture under reflux condensation for the period of one-half hour and acidifying by the addition of 2 normal hydrochloric acid, the mass is vaporized during stirring until it begins to gelatinize. At this point the resin is dissolved in alcohol in equal proportions.

In order to form the mixed resin, 100 parts of the dihydroxy diphenyl dimethyl methane resin is mixed with 100 parts of the 50% solution of urea resin and the resulting solution is heated to 60° to 70° C. for a short period of time. To this solution there is added 16 parts of a 10% solution of sulfuric acid in butanol and 5 parts of lactic acid ethyl ester as a softening agent. The resulting resin solution is particularly suitable as an adhesive in joining various materials as, for example, pressed sheets having as their basis either phenol or carbamide resin.

Example 4

Cresol is condensed with formaldehyde with the aid of barium hydroxide as a catalyst until the cresol dialcohol step is reached. The resulting resin is then dissolved in butanol and the barium is precipitated from this solution in the form of its carbonate by means of carbonic acid, the precipitate being finally removed by filtration. Then the butanol is partially distilled off under vacuum until a 50% resin solution is obtained.

200 parts of formaldehyde in 30% aqueous solution and 200 parts of butanol are heated to boiling and to the boiling solution there is added, within a period of 1 hour, a solution composed of 60 parts of urea, 1 part of monosodium phosphate and 60 parts of water. The resulting reaction product is distilled at 50° to 60° C. until sufficient liquid is evaporated off to produce a mass of syrupy consistency. The resulting product is then dissolved in 160 parts of ethyl alcohol and 40 parts of benzyl alcohol.

100 parts of the resulting cresol resin solution are mixed with 100 parts of the urea resin solution and a suitable dye is ground into the mixture, thereby forming a coating composition of the nature of an enamel. After the addition of 10 parts of a 10% hydrochloric acid solution, the coating composition is ready for use. The applied film quickly dries to produce a hard, shiny and resistant film.

It should be understood that the instant invention is not limited to the particular procedures herein described, nor the specific compounds disclosed, for it extends to all equivalent methods and materials within the scope of the claims appended hereto.

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