

# ALIEN PROPERTY CUSTODIAN

## SYNTHETIC RESINOUS PRODUCTS AND PROCESS OF PRODUCING THE SAME

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This invention relates to synthetic resinous products and to processes of producing the same. More specifically it relates to resin masses composed of a combination of a condensation resin of the phenol-aldehyde type with a polymerized resin of the polyvinyl acetal type.

Condensation resins as produced from phenols and carbonyl compounds when in the final stage of reaction possess a number of excellent properties, including high stability against the action of heat, insolubility, infusibility, and also a substantial inertness to the action of various chemicals. These resins, however, have several undesirable properties, among which may be mentioned particularly low elasticity qualities and low resistance to breaking under blows when bent or under strain.

Polymerization resins derived from vinyl compounds, which are non-hardening and thermo plastic in character, have very good elasticity properties, and some of such resins, besides having very good flexibility, have a substantial resistance to breaking under blows when bent or under strain, these properties excelling by far those of the phenol resins. These polymerization resins, however, are not satisfactory for many purposes, primarily because of their low stability against heat, their ready solubility or tendency to swell in organic solvents, and in certain instances, their sensitiveness to water and alkalies.

The deficiencies of these two types of resins have been known for some time, and many attempts have been made to overcome the same by combining various polymerization resins with the condensation resins. For example, various mixtures of such resins have been proposed for use in the production of abrasive articles of greater elasticity, the mixed resins being used as a binder for the abrasive substance. Among the polymerization resins suggested for this use are polystyrol, its homologues and derivatives, polymeric organic and inorganic vinyl esters, vinyl ethers and acrylic derivatives. Although many of these mixed resins are superior in certain respects to the individual resins, they are not completely satisfactory for many uses.

An object of the present invention is to produce new and improved resins free of the hereinbefore mentioned inferior properties, and to produce resins having among other properties low solubility in organic solvents, substantial resistance to water and high flexing properties.

Broadly considered, the process of the present invention involves the formation of new resins by reacting condensation resins, such as resols and

novolaks, with functional derivatives of polyvinyl alcohols, such as whole or partial acetals of wholly or partially hydrolyzed polyvinyl esters. The polyvinyl component, which resinifies by an inter-  
5 action in some manner within the mass, is derivable by condensing an at least partially hydrolyzed polyvinyl ester with a carbonyl compound, such as with formaldehyde, forming polyvinyl formaldehyde acetal.

The formation of mixed esters is preferably brought about through the action of heat at a raised temperature adapted to cause a homogeneous resinous product to form, the reaction being assisted through a mechanical mixing apparatus,  
10 which may be a mixing roller, a kneader, a screw mixing device, or a spiral mixing device. In some embodiments, reaction and mixing is preferably facilitated through the use of solvents for the individual resin components. In some instances,  
15 it is preferable to employ a hardening agent or hardening accelerator of a conventional or other type for advancing the condensation reaction.

In accordance with one embodiment of the process, the basic or raw materials for the formation of the condensation resins, that is the phenolic component, is mixed with the derivative of the polyvinyl alcohol such as polyvinyl formaldehyde acetal, and then reacted with an aldehyde such as formaldehyde. In accordance with another  
20 embodiment, the phenolic compound is mixed with the wholly or partially hydrolyzed polyvinyl ester, and both of such compounds are then reacted with an aldehyde or mixture of aldehydes, optionally in the presence of a catalyst, conventional hardening catalysts being satisfactory. Under this procedure the formation of the raw resins and the reaction between the same is  
25 effected in a single operation.

The following examples illustrate various possible procedures for carrying out the invention, the parts therein being by weight.

### Example 1

Two parts of a phenol formaldehyde condensation product obtained by condensing phenol and formaldehyde under alkaline conditions in a molar ratio of 1:1, and dissolving to form in 50% alcoholic solution, are reacted with one part of a polyvinyl ester acetal obtained according to  
30 known procedure from polyvinyl acetate (of which an 8.6% solution in benzol possessed a viscosity of 122 cp) and formaldehyde in the form of a 50% acetic acid solution. The resin mixture which precipitates is then washed and dried. This  
35 resulting mass may then be molded at a tempera-

ture of 170°-180° C. to form an excellent resin of outstanding toughness and mechanical resistance.

Its resistance to bending increased by 480% to 1400 kg/cm<sup>2</sup> as compared with that of the condensation resin, and increased by 17% as compared with the polyvinyl acetal alone. The resistance under bending to blows shows an increase of 540% to 32 cmkg/cm<sup>2</sup> as compared with the condensation resin alone. The absorption of water by the new resin after remaining in water for four hours at a temperature of 96°C. amounted to only 1.5% as compared with 15% for the polymerization resin itself.

#### Example 2

The resin components mentioned in Example 1 are produced as therein described, but the ratio is changed such that the mixture is composed of 80 parts of the condensation resin to 20 parts of the polymerization resin. The resulting new resin possesses a bending resistance increased by 520% to 1490 kg/cm<sup>2</sup>, and a bending resistance to blows by 320% to 21 cmkg/cm<sup>2</sup>, both as compared with the condensation resin. The absorption of water amounts to only 6% of that of the polymerization resin.

#### Example 3

Two parts of a resol, obtained by condensing one mol of dihydroxy diphenyl dimethyl methane with from 3 to 4 mols of formaldehyde in the presence of an alkali, are worked with one part of a polyvinyl acetal in the presence of a solvent for the acetal on a mixing roller at a temperature of 100°-120°C. As compared with that of the condensation resin, the bending resistance of the new resin increased by 50% to 1500 kg/cm<sup>2</sup>, resistance to bending under blows remained unchanged at 22-25 cmkg/cm<sup>2</sup> and the water absorption amounted to only 0.4%, which is equivalent to 3.6% of the capacity of the polymerization resin component.

#### Example 4

Two parts of a resol, such as described in Example 3, are worked in the absence of any solvent on a roller with one part of a commercial grade of a low viscosity acetaldehyde acetal of polyvinyl alcohol (having a viscosity when in the form of a 8.6% benzol solution of polyvinyl acetate equal to 4.0cp). Due to the low molecular weight of the product produced, this specific resin is not appreciably improved as to its toughness or mechanical resistance, but its absorption of water amounts to only 0.9%, and its absorption of ethyl alcohol after 48 hours at a temperature of 24°C. amounts only to 0.14%, which properties are quite an improvement as compared with the polyvinyl acetal used, such acetal itself being sensitive to water and easily dissolved in alcohol.

#### Example 5

Equal parts of a non-hardening phenol resin of the novolak type and polyvinyl formaldehyde acetal are worked as in Example 3 in the presence of 15% of a hardening agent, preferably hexamethylene tetramine, the percentage being calculated upon the weight of the condensation resin. The bending resistance of the new resin is increased by 30% to 1630 kg/cm<sup>2</sup> and the bending resistance to blows by 300% to 46 cmkg/cm<sup>2</sup>.

#### Example 6

Two parts of the phenol resin mentioned in Example 5 are reacted in the absence of a solvent

with one part of polyvinyl formaldehyde acetal obtained in conventional manner from polyvinyl acetate, an 8.6% benzol solution of which possesses a viscosity of 13 cp. The final resin obtained possesses a bending resistance which is increased by 7% to 1280 kg/cm<sup>2</sup> and a bending resistance to blows by 160% to 31 cmkg/cm<sup>2</sup>. The absorption of water by the resin amounted to 1.64%. Its heat stability at 112° C., in accordance with Martens, is somewhere between that of the raw materials (58° and 165°C.).

The proportions of the raw materials usable in the practice of the present invention may be varied within wide limits and no numerical value can be given therefor. The ratio of the polymerization resin components to the soluble fusible condensation resin components is controlled in any specific operation of the process by the demands to be put upon the intermediate or the final resin mass.

The resinous masses resulting from the above processes may be readily molded at conventional elevated temperatures to obtain synthetic resinous articles possessing an exceptional mechanical resistance. The molding operation, alternatively, may be effected by forming a homogeneous mixture of the raw materials directly in the mold and reacting the same therein, but if this procedure is followed, a longer period is necessary for the molding operation to make up for the lack of reaction accomplished through working on the hot roller or in the kneader.

The exact chemical constitution of the resinous masses produced in accordance with the present invention is not known, but the properties of the resins, such as their insolubility in organic solvents and their increased bending resistance, warrant the assumption that the mixed condensation resins with the polyvinyl acetals, which possess numerous free groups capable of reaction, have been reacted together to form a new chemical compound, or a mixture of new chemical compounds which differ from those heretofore known. The two above mentioned properties could not arise, under any known reasoning, from a mere mixture of the two known types of resin. Furthermore, condensation resins in solution with polyvinyl acetals are partly incompatible in that they precipitate each other, and even if the condensation resin is in molten condition, the acetal resin is not dissolved at the commencement of the reaction. It should be understood, however, that the invention is not to be limited by any theory of reaction, but that it includes the resinous masses resulting from the processes herein disclosed wherein the homogeneous masses having the appearance of single resins are produced. From the fundamental difference in properties between the new resins and the old individual resins, it is evident that interaction of some kind occurs.

The resins produced in accordance with the present invention do not possess the undesirable properties of the polymerization resin itself, such objectionable qualities to a large degree having been overcome. For example, the solubility in organic solvents has almost completely disappeared, sensitiveness to water is substantially reduced and stability under heat is considerably enhanced. As compared with the condensation resin employed, the new resinous mass is also considerably improved with reference to resistance to bending under blows. The most outstanding quality of the new resins is their resistance to bending, which is far superior to that of each of the com-

ponent resins. This quality is not obtained when condensation resins are combined with the polyvinyl resins hereinbefore described.

By suitable choice of raw materials or reaction components, the properties of the final resin masses such as flexibility, hardness, bending resistance and resistance to bending under blows may be varied to a large extent and made to produce resins of specific properties to suit special uses. The instant process is economical in operation in that any scrap resin remaining from prior molding processes may again be used because of the partially still existing thermo plastic properties.

The new resins may be used as such or in conjunction with conventional or other fillers, and with pigments. In accordance with known processes, they may be shaped with the aid of heat and pressure, as by molding or extruding. They

may also be projected between rollers to form films, bands and the like. Furthermore, they may be used as a coating for substantially all types of materials, as paints and lacquers, as electrical insulating materials, in various forms, and as impregnation agents and textile assistants, the last mentioned uses being of particular importance. The new resins are also adapted for many binding purposes, such as in the preparation of grinding wheels and brake shoes. They may also be manufactured in the form of and employed as adhesives and putties.

It should be understood that the instant invention is not limited to the specific compounds and procedures herein described, but it extends to all equivalents within the scope of the claims appended hereto.

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