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(54) CURED, POROUS POLYESTER RESIN AND METHOD FOR OBTAINING SAME

(71) We, AMERICAN CYANAMID COMPANY, a corporation organized and existing under the laws of the State of Maine, United States of America, of Berdan Avenue, Township of Wayne, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a micro-porous, polyester resin product from which water has been removed.

It is long known that water can be removed from certain cured polyester resinous products. In one process as exemplified by United States Patent No. 2,443,735, issued June 22, 1948, there is disclosed the addition of compatible emulsifiers to polyester resins prior to emulsion polymerization for purposes of stabilizing the emulsion, effecting compression molding, and removing water therefrom by drying the same. Such emulsifiers include the amyl, hexyl or octyl sulfosuccinic acid diesters and salts thereof. Moreover, the use of polymeric materials, such as polystyrene as an emulsifier to assist in drying, has also been disclosed in United States Patent No. 3,256,219, issued June 14, 1966. Unfortunately, none of these procedures is entirely satisfactory for the reason that not all, but rather substantially less than all, the water is initially eliminated from a cured, molded polyester product when dried. Subsequently, upon elimination of additional quantities of occluded water over a long period of time, say six months or a year, the eliminated water will cause the molded structure to lose its original definitions. Thus, the dried molded structure is said to lack integrity. If substantially all the water can be removed immediately subsequent to curing so that a molded structure does not lose its

water and, therefore, its integrity, such a procedure would fulfill a long-felt need in the art.

To this end, it has been found, unexpectedly, that the incorporation of small, but effective, amounts of an alkali metal salt of the sulfosuccinate diester of a monohydric alcohol of from 10 to 18 carbon atoms, when incorporated prior to emulsion polymerization of an unsaturated polyester resin, causes the resultant water-in-oil emulsion to become unstable. As such, substantially all, if not all, the water may be rapidly removed after gelation or curing occurs. The resultant resinous product possesses good to excellent integrity and there is a reduced or no tendency to distort with time due to gradual water removal.

Thus, the present invention provides a process for obtaining a cured, microporous, polyester resin from which water has been removed, comprising (1) adding to 60 to 40 parts by weight of a mixture of 20% to 60% by weight styrene and correspondingly 80% to 40% by weight of an essentially linear, ethylenically unsaturated polyester resin which is the reaction product of a dicarboxylic acid, optionally with a minor portion of a polycarboxylic acid containing three or more carboxyl groups, or an anhydride of said acid(s), and a dihydric alcohol, optionally with a minor portion of a polyhydric alcohol containing three or more hydroxyl groups, (a) from 40 to 60 parts by weight of water, (b) a polymerization catalyst (c) as emulsifier at least 0.1 by weight, based on the weight of the resin mixture, of an alkali metal salt of the sulfosuccinic acid diester of a monohydric, aliphatic alcohol containing from 10 to 18 carbon atoms; (2) agitating the resulting mixture to obtain a water-in-oil emulsion; (3) effecting cross-linking of the polyester resin with styrene; and

(4) thereafter removing substantially all of the water from the cross-linked resin.

It is found that, after curing of all resinous reaction product, substantially all the water, e.g. from 95% to 100%, can be removed from the cured product, for example by subjecting it to a temperature from 120°C. to 130°C. typically for from two to three hours.

The ethylenically unsaturated polyester resins employed in the practice of the present invention are all well known in the art and are prepared by reacting dicarboxylic acids, or their anhydrides, with dihydric alcohols. They are prepared using a procedure wherein at least one of the reactive components contains α,β -ethylenic unsaturation. By following this procedure, resinous, essentially linear esterification or condensation products containing a plurality of ethylenically unsaturated linkages distributed along the backbone of their polymer chains, are produced.

The use of α,β -ethylenically unsaturated dicarboxylic acids provides a convenient method of introducing ethylenic unsaturation into the polyester resins. It is preferred to employ such α,β -ethylenically unsaturated dicarboxylic acids as maleic, fumaric, citraconic, γ,γ -dimethylcitraconic, mesaconic, itaconic, α -methylitaconic, γ -methylitaconic and tetraconic, as well as mixtures thereof, but minor amounts of α,β -ethylenically unsaturated polycarboxylic acids containing three or more carboxyl groups, such as aconitic, together with the particular α,β -ethylenically unsaturated dicarboxylic acid or acid chosen, may also be used.

Whenever available, the anhydrides of any of the aforementioned α,β -ethylenically unsaturated polycarboxylic acids may be substituted for said acids in whole or in part.

Any of the large class of dihydric alcohols ordinarily used in preparing reactive polyester resins may be employed in the practice of the present invention. While saturated aliphatic diols are preferred as coreactants in the preparation of the polyester resins, it is not mandatory that all of the polyol used be of this type in that minor amounts, e.g., usually up to 10% of the total equivalents of hydroxyl groups present in the esterification mixture, of polyols having more than two hydroxyl groups, may also be employed.

Among the dihydric alcohols which may be employed are saturated aliphatic diols, such as ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, tetraethylene glycol, butanediol - 1,2, butanediol - 1,3, butanediol - 1,4, pentanediol - 1,2, pentanediol - 1,3, pentanediol - 1,4, pentanediol - 1,5, hexanediol - 1,2, hexanediol - 1,3, hexanediol - 1,4, hexanediol - 1,5, hexanediol - 1,6 and neopentyl glycol, as well as mixtures thereof.

Among the polyols having more than two hydroxyl groups which may be employed in minor amounts, together with the above-mentioned diols, are saturated aliphatic polyols, such as glycerol, trimethylol ethane, trimethylol propane, pentaerythritol, dipentaerythritol, arabitol, xylitol, dulcitol, adonitol, sorbitol and mannitol, as well as mixtures thereof.

Among the halogenated polyols that may be employed are 2,2'-chloromethylpropanediol - 1,3, adducts of hexachlorocyclopentadiene with unsaturated polyols, such as butenediols and pentenediols, and adducts of hexachlorocyclopentadiene with polyols having three or more hydroxyl groups, one of which is etherified with an unsaturated alcohol reactive with hexachlorocyclopentadiene. Among the latter are compounds such as 3 - [1,4,5,6,7,7 - hexachlorobicyclo - (2.2.1) - 5 - hepten - 2 - yloxy] - 1,2 - propanediol, which is the adduct of hexachlorocyclopentadiene with glycerol ether, 3 - [1,4,5,6,7,7 - hexachlorobicyclo(2.2.1) - hepten - 2 - yl] - methoxy - 1,2 - propane diol, which is the adduct of hexachlorocyclopentadiene with allyl glycerol, and adducts of hexachlorocyclopentadiene with vinyl and allyl ethers of pentaerythritol. Mixtures of these halogenated polyols may also be employed, if desired.

The esterification mixtures, from which the polyester resins employed in the practice of the present invention are prepared, are generally formulated so as to contain a stoichiometric balance between carboxyl and hydroxyl groups or small excess of hydroxyl groups. Thus, a diol and a dicarboxylic acid are usually reacted on at least a mol-to-mol basis. In common commercial practice, a small excess of polyol, usually in the range of from 5% to 15% excess, is employed. This is done primarily for economic reason, i.e., to ensure a rapid rate of esterification.

The polyester resins used in the practice of the present invention are formed in the manner customarily observed in the art. Thus, the particular polycarboxylic acid or acids and polyol or polyols employed are reacted at elevated temperatures and atmospheric pressure. Since resinifying reactants of this type are prone to develop undesirable color when in contact with air at elevated temperatures, it is generally considered good practice to conduct the esterification reaction in an inert atmosphere, such as can be obtained by bubbling an inert gas, e.g., carbon dioxide, nitrogen, and the like, through the esterification mixture. The reaction temperature is not critical; thus, the reaction will preferably be carried out at a temperature which usually will be just below the boiling point of the most volatile component of the reaction mixture, generally the polyol.

Preferably, the esterification mixture should be sufficiently reacted so as to ultimately produce a polyester resin having an acid number not more than 75. It is particularly preferred to employ polyester resins having acid numbers ranging from 10 to 30, or below.

Resultant polyester resin is next cut with from 20% to 60% by weight styrene. The so-diluted polyester resin is then emulsion polymerized in the presence of the emulsifier and a polymerization catalyst such as a peroxide e.g. hydrogen peroxide. A cobalt promoter and a compatible amine such as dimethyl aniline may be also added to the reaction mixture, as is known in the art. Preferably, the emulsifier is added initially followed by the addition of water containing the polymerization catalyst. Agitation of the mixture results in a water-in-oil emulsion. Curing takes place in the presence of the emulsifier. If the resin is to be molded it should be poured into a suitable mold prior to curing. If the product is too thick to pour, it is highly advantageous to incorporate small amounts of a viscosity reducer, namely, a mixed octadecyl-guanidine-amine polyoxyethanol.

It is good practice to incorporate from 0.1% to 5% of the emulsifier based on the total weight of the polyester resin and styrene. Usually, of from 0.3% to 0.6% is good operating range. Examples of emulsifiers particularly useful herein are the potassium salt of sulfosuccinate diester of decyl alcohol or undecyl alcohol or lauryl alcohol, the sodium salt of sulfosuccinate diester of tridecyl alcohol, the potassium salt of sulfosuccinate diester of myristyl alcohol, the lithium salt of sulfosuccinate diester of pentadecyl or stearyl alcohol, the sodium salt of sulfosuccinate diester of octadecyl alcohol, and mixtures of the same.

As previously stated, the viscosity of the polyester resin prior to cross-linking can be reduced by incorporating therein small amounts, typically from 0.1 to 2%, by weight based in the total weight of polyester resin and styrene, or a mixed octadecyl-guanidine-amine polyoxyethanol which is employed usually as a 70% aqueous solution.

Preparation of the polyester resin in about equal parts of water catalyzed with a suitable peroxide, such as hydrogen peroxide, and containing a compatible amine, such as dimethyl aniline and a cobalt compound is well known. However, without the incorporation of small amounts of specific emulsifier and, optionally, a specific viscosity reducer, rapid total water removal after gelation cannot be achieved.

Although it is normally preferred that the emulsifying mixture should contain equal amounts by weight of water and catalysed polyester resin, this is not a critical feature

of the process of the present invention and it is possible to vary the weight ratio of water to resin within the range from 40:60 to 60:40 respectively. The invention is illustrated by the Examples which follow. Unless otherwise stated, the parts are by weight.

Example 1

To 55 parts of styrene and 45 parts of a polyester resin prepared by esterifying at a temperature of about 225°C., 0.22 mol of dipropylene glycol, 2.95 mols of diethylene glycol, 3.10 mols of propylene glycol, 0.29 mol of adipic acid, 3.99 mols of iso-phthalic acid and 1.80 mols of maleic anhydride for a time sufficient to obtain an acid number between 10 and 15, are added one part by volume of cobalt, as a 12% solution of cobalt octoate and 0.4 part by volume of dimethyl aniline. To the latter styrene-resin mixture is admixed 0.4 part of the sodium salt of sulfosuccinate diester of tridecyl alcohol and 0.4 part of a mixed octadecyl-guanidine-amine polyoxyethanol. Resultant overall mixture is next emulsified with 100 parts of water containing one part of a 30% solution of hydrogen peroxide polymerization initiator. This emulsion is poured into a suitable mold. Gelation or cross-linking occurs within fifteen minutes after introduction into the mold and the molded article is removed. The latter article is then heated to a temperature from 120°C. to 130°C. for a period of three hours. It is found that 99% of the total water originally present in the resinous mixture is removed.

Comparative Example 1

Repeating the above Example 1 in every detail except the emulsifying mixture consisting of the sodium salt of the sulfosuccinic diester of tridecyl alcohol and the mixed octadecyl-guanidine-amine polyoxyethanol is omitted, there is removed a total of approximately 21% of the water present, leaving as a residue some 79% to 80% of water in the molded article.

Example 2

The procedure of Example 1 is repeated in every detail except that the sodium salt of sulfosuccinate diester of lauryl alcohol is substituted for the sodium salt of sulfosuccinate diester of tridecyl alcohol. Similar results with respect to water removal are observed.

Example 3

Repeating in every detail the procedure of Example 1, except that in the emulsifying mixture the mixed octadecyl-guanidine-amine polyoxyethanol is eliminated, there then results the removal of 95 to 99% water from the dehydrated molded article.

Example 4

The procedure of Example 1 is followed in every detail except that the polyester resin is prepared by reacting at a temperature of approximately 225°C. for a time sufficient to obtain an acid number between 10 and 14, 2.14 mols of ethylene glycol, 4.3 mols of propylene glycol, 2.90 mols of iso-phthalic acid, and 3.10 mols of maleic anhydride. There is removed approximately 99% of the water from the molded article.

Example 5

Repeating Example 1 in every detail except that the polyester resin is prepared by reacting 6.80 mols of diethylene glycol, 3.0 mols of iso-phthalic acid, and 0.60 mols of dimeric higher fatty acids (Emery Industries No. 4,050), and 2.40 mols of maleic anhydride to obtain an acid number of from 10 to 15. Since the resultant resin is exceedingly viscous, the sodium salt of sulfosuccinate diester of tridecyl alcohol content is increased to 1.4 parts and the mixed octadecyl-guanidine-amine polyoxyethanol is increased to 0.8 part. Approximately 95% of the water is removed from the molded article when dehydrated.

Comparative Example 2

In lieu of the emulsifying agents employed in Example 1 above, there is substituted therefor 0.3% of each of (a) a phenoxy resin PAHJ-obtained from Union Carbide, (b) "Bakelite" (Registered Trade Mark) RMD 4,500 obtained from Union Carbide, which resin is a copolymer of styrene and acrylonitrile, (c) polystyrene obtained from the Shell Chemical Company, and (d) the sodium salt of sulfosuccinate diester of octyl or nonyl alcohol. When dehydrated, losses of not more than 20% of the total water initially present were noted.

Example 6

The procedure of Example 1 above is repeated in every detail except that the potassium salt of sulfosuccinate diesters of decyl-, myristyl- or octadecyl alcohol is separately substituted for the corresponding sodium salt of the sulfosuccinate diester of tridecyl alcohol. Removal of more than 94% of the water from the cured resin at 120°C. to 130°C. within two to three hours is readily attained.

WHAT WE CLAIM IS:—

1. A process for obtaining a cured, micro-porous, polyester resin from which water has been removed, comprising (1) adding to 60 to 40 parts by weight of a mixture of 20% to 60% by weight styrene and correspondingly 80% to 40% by weight of an essentially linear, ethylenically unsaturated polyester resin which is the reaction product of a dicarboxylic acid, optionally with a minor portion of a polycarboxylic acid containing three or more carboxyl groups, or an anhydride of said acid(s); and a dihydric alcohol, optionally with a minor portion of a polyhydric alcohol containing three or more hydroxyl groups, (a) from 40 to 60 parts by weight of water, (b) a polymerization catalyst (c) as emulsifier at least 0.1% by weight, based on the weight of the resin mixture, of an alkali metal salt of the sulfosuccinic acid diester of a monohydric, aliphatic alcohol containing from 10 to 18 carbon atoms; (2) agitating the resulting mixture to obtain a water-in-oil emulsion; (3) effecting cross-linking of the polyester resin with styrene; and (4) thereafter removing substantially all of the water from the cross-linked resin.

2. A process according to Claim 1, in which the emulsifier is the sodium salt of the sulfosuccinate diester of tridecyl alcohol, or the potassium salt of the sulfosuccinate diester of decyl alcohol.

3. A process according to Claim 1 or Claim 2, in which from 0.1% to 5% of said emulsifier is added, based on the total weight of the unsaturated polyester resin and styrene.

4. A process according to any preceding claim, in which the water is removed by heating at a temperature of 120°C. 130°C.

5. A process according to any preceding claim, in which there is added in addition to said emulsifier from 0.1% to 2% by weight of a mixed octadecyl-guanidine-amine polyoxyethanol, based on the total weight of the unsaturated polyester resin and styrene.

6. A process according to any preceding claim, in which the unsaturated polyester resin has been prepared by reacting a mixture of ethylene glycol, iso-phthalic acid and maleic anhydride.

7. A process according to any one of Claims 1—5, in which the unsaturated polyester resin has been prepared by reacting a mixture of dipropylene glycol, diethylene glycol, propylene glycol, adipic acid, iso-phthalic acid, and maleic anhydride.

Example 4

The procedure of Example 1 is followed in every detail except that the polyester resin is prepared by reacting at a temperature of approximately 225°C. for a time sufficient to obtain an acid number between 10 and 14, 2.14 mols of ethylene glycol, 4.3 mols of propylene glycol, 2.90 mols of iso-phthalic acid, and 3.10 mols of maleic anhydride. There is removed approximately 99% of the water from the molded article.

Example 5

Repeating Example 1 in every detail except that the polyester resin is prepared by reacting 6.80 mols of diethylene glycol, 3.0 mols of iso-phthalic acid, and 0.60 mols of dimeric higher fatty acids (Emery Industries No. 4,050), and 2.40 mols of maleic anhydride to obtain an acid number of from 10 to 15. Since the resultant resin is exceedingly viscous, the sodium salt of sulfosuccinate diester of tridecyl alcohol content is increased to 1.4 parts and the mixed octadecyl-guanidine-amine polyoxyethanol is increased to 0.8 part. Approximately 95% of the water is removed from the molded article when dehydrated.

Comparative Example 2

In lieu of the emulsifying agents employed in Example 1 above, there is substituted therefor 0.3% of each of (a) a phenoxy resin PAHJ-obtained from Union Carbide, (b) "Bakelite" (Registered Trade Mark) RMD 4,500 obtained from Union Carbide, which resin is a copolymer of styrene and acrylonitrile, (c) polystyrene obtained from the Shell Chemical Company, and (d) the sodium salt of sulfosuccinate diester of octyl or nonyl alcohol. When dehydrated, losses of not more than 20% of the total water initially present were noted.

Example 6

The procedure of Example 1 above is repeated in every detail except that the potassium salt of sulfosuccinate diesters of decyl-, myristyl- or octadecyl alcohol is separately substituted for the corresponding sodium salt of the sulfosuccinate diester of tridecyl alcohol. Removal of more than 94% of the water from the cured resin at 120°C. to 130°C. within two to three hours is readily attained.

WHAT WE CLAIM IS:—

1. A process for obtaining a cured, micro-porous, polyester resin from which water has been removed, comprising (1) adding to 60 to 40 parts by weight of a mixture of 20% to 60% by weight styrene and correspondingly 80% to 40% by weight of an essentially linear, ethylenically unsaturated polyester resin which is the reaction product of a dicarboxylic acid, optionally with a minor portion of a polycarboxylic acid containing three or more carboxyl groups, or an anhydride of said acid(s), and a dihydric alcohol, optionally with a minor portion of a polyhydric alcohol containing three or more hydroxyl groups, (a) from 40 to 60 parts by weight of water, (b) a polymerization catalyst (c) as emulsifier at least 0.1% by weight, based on the weight of the resin mixture, of an alkali metal salt of the sulfosuccinic acid diester of a monohydric, aliphatic alcohol containing from 10 to 18 carbon atoms; (2) agitating the resulting mixture to obtain a water-in-oil emulsion; (3) effecting cross-linking of the polyester resin with styrene; and (4) thereafter removing substantially all of the water from the cross-linked resin.

2. A process according to Claim 1, in which the emulsifier is the sodium salt of the sulfosuccinate diester of tridecyl alcohol, or the potassium salt of the sulfosuccinate diester of decyl alcohol.

3. A process according to Claim 1 or Claim 2, in which from 0.1% to 5% of said emulsifier is added, based on the total weight of the unsaturated polyester resin and styrene.

4. A process according to any preceding claim, in which the water is removed by heating at a temperature of 120°C. 130°C.

5. A process according to any preceding claim, in which there is added in addition to said emulsifier from 0.1% to 2% by weight of a mixed octadecyl-guanidine-amine polyoxyethanol, based on the total weight of the unsaturated polyester resin and styrene.

6. A process according to any preceding claim, in which the unsaturated polyester resin has been prepared by reacting a mixture of ethylene glycol, iso-phthalic acid and maleic anhydride.

7. A process according to any one of Claims 1—5, in which the unsaturated polyester resin has been prepared by reacting a mixture of dipropylene glycol, diethylene glycol, propylene glycol, adipic acid, iso-phthalic acid, and maleic anhydride.



8. A process for obtaining a cured, microporous, polyester resin, according to Claim 1 and substantially as described in any one of the Examples herein.

5 9. A cured, microporous, polyester resin whenever obtained by a process according to any preceding claim.

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