

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF ARTIFICIAL RESINS

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The present invention relates to a process for the manufacture of artificial resins.

It is known that artificial resins can be prepared by heating urea-formaldehyde or thiourea-formaldehyde condensation products or such substances as are capable of forming such condensation products together with finished resins from polyvalent alcohols, namely glycol or glycerine, and polybasic acids in the presence of monovalent alcohols. In order to obtain soft resins of the said type it is necessary to employ condensation products from polyhydric alcohols, polybasic acids and monobasic fatty acids, as for example linoleic acid or ricinoleic acid. The resins so obtained, however, are sensible to light and temperature.

I have now found that soft, elastic artificial resins of good power of resistance to the action of light and temperature are obtained by heating low-molecular condensation products from a urea and/or thiourea and formaldehyde or the initial substances capable of forming the said condensation products to a temperature of from 100°C to 160°C, in the presence of monohydric alcohols together with weakly acid condensation products containing free hydroxy groups and being soluble in alcohols, from aliphatic (i.e. open-chain aliphatic or cycloaliphatic) dicarboxylic acids containing from 5 to 10 carbon atoms and trivalent alcohols or alcohols of higher valency containing more than 3 carbon atoms in the molecule, until appreciable quantities of water are no longer split off, but the resulting resins are still readily soluble.

Suitable open-chain aliphatic or cycloaliphatic dicarboxylic acids with at least 5 carbon atoms in the molecule are for example glutaric acid, adipic acid, pimelic acid, ketopimelic acid, sebacic acid and cyclohexanediacetic acid. Among suitable trivalent or higher valent alcohols containing more than 3 carbon atoms in the molecule may be mentioned, for example, trimethylolethane, trimethylpropane, pentaerythrite and hexanetriol. Mixtures of several of the said dicarboxylic acids and/or polyhydric alcohols may also be employed. The condensation products from the said aliphatic dicarboxylic acids and polyhydric alcohols must not be strongly acid, as otherwise premature gelatinization would occur and because strongly acid constituents are undesirable in resins to be used as a coating agent. The acid number should not be higher than about 40, preferably it should be in the range up to 30. Condensation products from the aliphatic dicarboxylic acids and the polyhydric alcohols which are faintly acid and

soluble in alcohol are obtained by heating mixtures of the initial materials at not too high temperatures, preferably at 135° to 250°C.

The low-molecular condensation products from urea and/or thiourea and formaldehyde are made by known methods, preferably in a basic medium. The simultaneous employment at this stage of a monohydric alcohol is advantageous. The condensation products or their constituents forming such products, are then heated, in the presence of a monovalent alcohol and the condensation products from the dicarboxylic acids and polyhydric alcohols as described, at a temperature of between 100° and 160°C. It is advantageous to use monohydric alcohols with a boiling point above 100°C, as the water formed in the condensation or introduced by the aqueous formaldehyde may then be removed with special ease by distillation. When appreciable quantities of water are no longer split off, the condensation is discontinued. The resulting resin is then obtained in the form of an alcoholic solution.

The resins are eminently suited for the production of baking varnishes. The coatings obtained with the said resins are very light in colour and extremely fast to temperature and light. The varnishes can be caused to dry already at ordinary or slightly raised temperatures by an addition of acid hardeners, as for example strong acids, as hydrochloric acid, formic acid, chloroacetic acid, sulphosalicylic acid and lactic acid, or acid esters, as maleic acid monomethyl ester, or substances capable of splitting off acid, as benzenesulphochloride and toluenesulphochloride. These different possibilities of effecting their drying renders it possible to use the resins in different manner in the lacquer industry. Baking varnishes prepared therefrom may be applied with special advantage for example onto metals. The varnishes are distinguished by a good adherence to light metals. By virtue of their extremely high elasticity they may even be employed for coating thin metal foils.

Materials sensible to the influence of higher temperatures may preferably be coated with the resins in admixture with one of the said acid hardeners. Thus, for example, extremely elastic coatings on wood, paper, textiles, leather and similar materials may be obtained, the products thus obtainable being useful as artificial leather, oil-cloth, oil skin (oil silk) and patent leather (Japanned leather). The elasticity and the gloss of the coated products may be influenced at will by varying the proportion of the condensation products from the aliphatic dicarboxylic acids and

polyhydric alcohols and the urea- or thiourea-formaldehyde condensation products in the resins. The higher the percentage in condensation products from the said dicarboxylic acids and polyhydric alcohols, the higher generally is the gloss and the elasticity.

By baking as well as by hardening the resins in the presence of acid hardeners, the resins and hence the coatings prepared therefrom are rendered to a far-going degree insoluble in the usual organic solvents. The varnishes in the hardened condition are also distinguished by a good resistance to dilute lyes, acids and salt solutions.

The following Examples will further illustrate how the present invention may be carried out in practice, but the invention is not restricted to these Examples. The parts are by weight.

Example 1

292 parts of adipic acid are heated together with 400 parts of trimethylolethane while stirring at 250 to 280° C until about 120 parts of water are distilled off which is the case after about 1 hour. The reaction mixture is then allowed to cool and is diluted with alcohol to form an about 70 per cent solution. The acid number of the resinous product thus obtained is 9.

In a vessel provided with a reflux condenser, means for removing volatile parts by distillation and a stirring device 480 parts of paraformaldehyde and 384 parts of urea are dissolved in 2000 parts of ethyl alcohol while adding 48 parts of 25 per cent aqueous ammonia. The whole is heated for an hour under reflux and 1050 parts of the 70 per cent solution of the adipic acid-trimethylolethane resin obtained according to paragraph 1 are added. The mixture is further heated to boiling and the reflux cooling is so regulated that 1500 parts of alcohol distill off slowly together with the major part of the water formed during the reaction. Fresh alcohol is added and the removal of the water together with alcohol is continued until the mass is practically free from water. The product is then diluted with alcohol to form an about 50 per cent viscous solution which as such or after the addition of nitrocellulose, resins and other film-forming substances is suitable as an adhesive.

Example 2

110 parts of the 70 per cent alcoholic solution obtained according to Example 1, paragraph 1, are diluted with 180 parts of normal butanol. 90 parts of dimethylol urea and 15 parts of paraformaldehyde (or trioxymethylene) are added and the whole is condensed by heating for about 10 hours while distilling off alcohol, water and butanol. After adjusting the concentration of the solution to 50 per cent it is filtered in order to remove any parts causing turbidity. The solution is suitable as an adhesive and can also be employed for lacquering purposes. For the latter purpose pigments, such as titanium white, aluminium bronze and the like, may be added and the desired viscosity may be obtained by dilution. Such lacquers are suitable especially for metallic surfaces including light metal surfaces. The lacquers may be brushed or sprayed. After evaporation of the solvent the coatings obtained are preferably baked at 150° C. They possess excellent elasticity, hardness and fastness against scraping; they are very fast to light and do not yellow even at higher temperatures. If the lacquers are baked at about 180° C the coatings are also stable against corrosion by motor fuels.

Example 3

792 parts of a mixture consisting of hexanetriol and octanetetrol (obtained as a residue in the distillation of 1,3-butylene glycol formed by hydrogenation of commercial aldol) are heated for 5 hours together with 584 parts of adipic acid at about 240° C. A soft resin having an acid number of 10 is formed while 148 parts of water are separated.

120 parts of the said resin are dissolved in 160 parts of amyl alcohol. 40 parts of urea and 180 parts of 40 per cent formaldehyde are added and the whole is heated for 3 hours at 95° C while stirring. The volatile parts are distilled off until a residue of 310 parts is left. A resin is obtained which after dilution, for example with 70 parts of amyl alcohol, may be employed in the same manner as the resin obtainable according to Example 2.

Example 4

130 parts of glutaric acid are heated together with 300 parts of trimethylolpropane for about 10 hours at 200° C. A soft resin of the acid number 1.5 is obtained.

Instead of glutaric acid the equimolecular proportion of adipic acid may be employed. Higher amounts of dicarboxylic acids, for example 300 parts of adipic acid, may also be employed instead, resins of higher acid number thus being obtained (in the case of 300 parts of adipic acid the acid number is about 28). By working in vacuo the reaction period may be considerably shortened.

A mixture of 735 parts of 30 per cent formaldehyde, 192 parts of urea, 25 parts of hexamethylene tetramine and 960 parts of normal butanol is heated for about 1 hour to boiling while reflux cooling. 400 parts of one of the resins obtainable according to paragraphs 1 and 2 are added and the whole is heated to boiling while distilling off water and butanol and recycling the latter until practically no water distils off. The product obtained is preferably diluted with normal butanol to form a 50 per cent solution.

75 parts of the said solution are mixed with 30 parts of alcohol and 8 parts of a 5 per cent solution of benzene sulfochloride in alcohol. The mixture thus obtained is brushed or sprayed onto wood. The lacquer is dry already after 2 hours and after 10 hours it is completely hardened. Without the addition of benzene sulfochloride it can be stored for any desired period. Without the said addition the lacquer may also be hardened by baking. The lacquer is compatible with pigments whether it contains the said hardening agent or not. It is also very suitable as a binding agent for abrasive papers fast to water and benzine.

100 parts of the resin disclosed above are mixed with a solution of the equal amount of the glutaric acid (or adipic acid) -trimethylolpropane condensation product which has been employed for the preparation of the resin in 200 parts of butanol. After diluting the mixture with 25 parts of alcohol and 25 parts of toluene and adding 2 parts of a 1 per cent methyl-alcoholic hydrochloric acid solution a lacquer is obtained which (if desired after further dilution) may be sprayed on a thin natural silk fabric yielding an excellent oil-skin which is suitable for electrical isolating purposes and as a water-tight fabric. It is possible to apply several coatings of the said kind, each coating being allowed to

harden for a short period and if desired each coating being polished before applying the next one. Oil-skin thus obtained does not show the undesired property of becoming soft and sticky (syneresis) as is the case with oil-skin prepared by means of drying oils in consequence of a decomposition of the said oils; it is fast to light and stable to oils, fats and motor fuels.

The lacquer solution is suitable for example for impregnating pipes of flexible material or linen for tents. If about 10 per cent of titanium white are added to the lacquer and it is brushed onto fabrics excellent oil cloth and artificial leather can be obtained. Frequently it is advantageous for this purpose to prime the fabrics with an aqueous dispersion of polyvinyl compounds.

The lacquers are suitable also for the preparation of japanned leather. The lower layers of

the lacquer are preferably produced by means of relatively soft resins of the type in question. In view of the colorlessness of the binding agent it is suitable to produce even pure white japanned leather.

Example 5

538 parts of a 50 per cent normal butanol solution of a urea-formaldehyde condensation product produced in the presence of butanol are heated for 3½ hours at 135 to 140°C in a pressure-vessel together with 394 parts of a condensation product from trimethylolpropane and adipic acid produced according to Example 4. A solution is thus obtained which is excellently compatible with pigments and which dries with high gloss. The solution is suitable for producing lacquers to be baked.

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