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INTERPOLYMERIZATION PRODUCTS

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The present invention quite generally relates to new and valuable interpolymerization products which may be obtained by polymerizing a mixture of about 90 per cent to about 98 per cent of a vinyl ester of an organic carboxylic acid with about 2 to about 10 per cent of a compound of the following formula:

$$CH_2=\underset{R_1}{C}=\underset{R_2}{C}-COOH$$

wherein R_1 and R_2 stand for a substituent of the group consisting of hydrogen, methyl and chlorine. These interpolymerization products are a valuable new type of synthetic resins the properties of which are not inferior, as might be expected, but are superior to those of the polyvinyl esters themselves. For instance the softening point of the interpolymerization product of vinyl acetate and crotonic acid ester is not decreased, as compared with that of polymerized vinyl acetate, but increased, that is, the resistance to heat is improved. Furthermore the interpolymerization product is more resistant to water and atmospheric conditions than is the polymerization product from polyvinyl acetate alone. Since crotonic acid and its derivatives containing free carboxylic acid groups are not capable of being polymerized alone, the present process involves the great advantage that the polymerization product is always a complete interpolymerization product for none other than the interpolymerization products can be formed; whereas, in the case of interpolymerization products of two components each of which can be polymerized alone, uniformity of product cannot be obtained unless the most favorable conditions are carefully observed, or even then.

The new artificial resins are insoluble in water, whereby they are advantageously distinguished from those interpolymerization products which are obtainable from mixtures containing more than 10 per cent of crotonic acid. Such products prepared from large portions of crotonic acid have at least a swelling power in water. When being mixed with alkalies, such as potassium hydroxide, sodium hydroxide, lithium hydroxide and ammonium hydroxide and potassium carbonate, sodium carbonate, lithium carbonate and ammonium carbonate, or with organic nitrogen bases, such as monomethylamine, dimethylamine and trimethylamine and monoethylamine, diethylamine and trimethyl amine, ethanolamine or triethanolamine, the new resins yield salts which are soluble in water. The aqueous salt solutions thus obtained are particularly valuable for industrial purposes, since, on drying, they yield films which, if ammonia or bases volatile at room temperature are used as salt-forming components, become resistant to water already at room temperature. The films obtained from other salts may be rendered resistant to water by heating. By using a quantity of crotonic acid of less than 2 per cent for the preparation of interpolymerization products, there exists the danger that the interpolymerization products do no longer sufficiently dissolve or at least swell in aqueous alkalies.

The polymerization is performed by the known methods of polymerizing particularly those applied to vinyl esters. There may be present a solvent or an indifferent diluent; the polymerization may also occur in an emulsion. In order to accelerate the reaction, heat or light may be used as well as a catalyst, for instance a peroxide. It is suitable to apply less than about 1 mol of crotonic acid or the derivative thereof per about 1 mol of the readily polymerizing ester.

As vinyl esters of organic carboxylic acids there may be used: vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl chloracetate, vinyl butoxacetate, vinyl benzoate, vinyl stearate. As the other component there may be applied: crotonic acid, bete-chlorcrotonic acid, alpha-methylcrotonic acid, beta-methyl crotonic acid.

There may likewise be polymerized two, three or more of the vinyl esters named above in mixture with the crotonic acid or one of the derivatives thereof named above.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto, the parts are by weight:

(1.) A solution of 10 parts of crotonic acid in 90 parts of vinyl acetate to which 0.5 part of benzoyl peroxide has been added is caused to run in the course of 4 hours into a glass flask provided with a reflux condenser and a feed vessel and heated in a water bath to 80° C–85° C. The mass becomes more and more viscous while a strong reflux takes place. After all of the solution has been introduced, the whole is further heated for 12 hours. The entire content of the flask has solidified to a colorless, hard block. After cooling the glass flask is broken and the block is mechanically comminuted to small pieces. The product dissolves in organic solvents, such as methanol or ethyl acetate to form a highly viscous solution; furthermore it dissolves in aqueous alkalies, such as ammonia or sodium carbonate, with formation of salt.

(2.) A solution of 86 parts of vinyl acetate, 10 parts of vinyl benzoate, 4 parts of crotonic acid and 25 parts of methanol to which 0.75 part of benzoyl peroxide has been added as an accelerator is heated to boiling in an enameled vessel provided with a reflux condenser and a stirring device. While refluxing, a vigorous polymerization of the solution sets in, and the solution becomes more and more viscous. After 10 hours the polymerization is complete. The product may be worked up by precipitation with water and a subsequent drying and is then soluble in aqueous alkalies. The concentrated methanol solution may also at once be brought to the desired concentration ready for used without treating it with any quantities of water and the portion calculated of alkali, such as ammonia. The solution may be used as a substitute for aqueous solutions of shellac for sizing and finishing purposes.

(3.) 100 parts of an aqueous solution of 0.1 per cent strength of the ammonium salt of an interpolymerization product from styrene and maleic anhydride are heated to 80°C in a heatable stirring vessel provided with a reflux condenser. A mixture of 95 parts of vinyl acetate and 5 parts of crotonic acid containing 0.5 part of orthotolylperoxide as a catalyst is slowly added thereto, while stirring. After about 4 hours the polymerization is complete. This is evident by the fact that the reflux ceases and the temperature in the reaction room rises. The mixture is then allowed to cool, while stirring. The pearly interpolymerization product which has separated is filtered, washed and dried at 30° C–40° C. The uniformly fine pearls readily dissolve in ammoniacal water without any residue.

(4.) 400 parts of an aqueous solution of 3 per cent strength of an addition product from oleyl alcohol with 16 mols of ethylene oxide, 4 parts of potassium persulfate and 2.6 parts of sodium vinylsulfonate are heated to 75° C in an enameled vessel provided with a reflux condenser and a stirring device. 465 parts of vinyl acetate, 120 parts of vinyl stearate, 15 parts of crotonic acid and 0.6 part of benzoyl peroxide are then caused to run in, while slowly stirring. After 5 hours the reflux ceases. Heating is continued for 1 hour and the mass is then allowed to cool, while stirring. A creamy, stable emulsion of an average viscosity is obtained which may readily be thickened with ammonia. After drying, a brilliant, elastic film of good water-repellent properties is thus obtained.

(5.) A mixture of 90 parts of N-butoxy-acetic acid vinyl ester, 10 parts of crotonic acid and 1 part of benzoyl peroxide is heated for 15 hours to 70° C to 80° C. 1 part of benzoyl peroxide is then further added and the whole is heated for 15 hours to 90° C to 95° C. The soft resin obtained is soluble in methanol, ethanol, acetone, ethyl acetate, glacial acetic acid, glycol formal, methylene chloride and benzene but insoluble in benzine or petroleum ether. By heating it with an aqueous solution of sodium carbonate of 10 per cent strength the sodium salt of the interpolymerization product is formed as a soapy mass soluble in water.

(6.) A mixture of 70 parts of vinyl acetate, 20 parts of vinyl stearate, 10 parts of crontonic acid, 0.25 part of formic acid and 1 part of benzoyl peroxide is heated for 15 to 20 hours to 70° C to 80° C. A colorless, solid resin is formed soluble in methanol, ethanol, acetone, acetic acid ethyl ester, methylene chloride, glycolformal and in dilute aqueous solutions of ammonia, sodium carbonate and caustic soda solution.

This application is a continuation-in-part of the application Serial No. 203,608 filed April 22, 1938.

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