

ALIEN PROPERTY CUSTODIAN

POLYMERIZATION PROCESS

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This invention relates to the polymerization of vinyl acetate; more particularly, it is directed to certain improvements in the preparation of vinyl acetate polymers whereby the characteristics of the polymeric products obtained are modified and the procedural steps involved are simplified.

It has been known heretofore that vinyl acetate may be polymerized by the action of heat and/or pressure and/or actinic radiation, and that the polymerization may be accelerated by the addition of polymerization catalysts, of which the most important are inorganic peroxides, such as hydrogen peroxide and per salts, and organic peroxides such as benzoyl peroxide.

It is also known that a number of chemical agents, of which hydroquinone and nitrobenzene may be mentioned as typical, exert an inhibiting action on the polymerization of vinyl acetate. It has been a common practice to add polymerization inhibitors of this character to monomeric vinyl acetate in order to prevent polymerization during storage, the inhibitors being eliminated by fractional distillation or other means prior to carrying out the polymerization operation.

I have now discovered that agents generally known to be polymerization inhibitors, when added to vinyl acetate in very minute proportions, produce an entirely different effect than that produced by the addition of these agents in the usual inhibiting amounts. When added in the very small proportions contemplated by the present invention, I have found that these agents do not function to inhibit polymerization materially, but in many cases actually serve to promote it substantially. Thus, by the proper selection of the inhibitor and the quantity of it used, it has been found that the induction period usually required for the polymerization to start, and the total time required for completion of the polymerization, can be appreciably shortened. This results in savings in heat requirements and labor and supervision costs, and in an increase in the productive capacity of the manufacturing equipment. Moreover, in certain instances, smaller amounts of the polymerization catalyst may be used than in the usual polymerization method, with corresponding savings in catalyst costs. Perhaps the most important advantage of the new method, however, resides in the fact that the characteristics of the polymeric products are substantially modified by the presence of the addition agents and it is thus possible to produce products having certain special properties which are not obtainable by methods heretofore known.

In carrying out the polymerization of vinyl acetate in the presence of polymerization inhibitors in accordance with the present invention, any of the usual polymerization procedures known to the art may be employed. Solvents for the monomer and/or polymer may be present or absent, and the polymerization may be effected by the action of actinic light by heat, preferably promoted by the action of polymerization catalysts. The present invention, however, has special advantages as applied to the so-called emulsion polymerization method wherein the monomeric vinyl acetate is emulsified in a non-solvent medium and then polymerized to form a latex-like emulsion of the polymer. An aqueous medium containing a partially saponified polyvinyl acetate having a saponification number of 80 to 180 and preferably from 120 to 130, as an emulsifying agent has been found to be a particularly satisfactory medium for this purpose although, of course, other media and emulsifying agents may be used. By the addition to the vinyl acetate of minute amounts of polymerization inhibitors there is effected a considerable reduction in the particle size of the emulsified polymer for a given concentration of emulsifying agent. This makes it possible to prepare latex-like emulsions of high stability even though relatively small amounts of emulsifying agent are used. Similarly, the addition of polymerization inhibitors in accordance with the present invention may be used to advantage in the so-called granular dispersion method of polymerization, wherein the monomeric vinyl acetate, instead of being emulsified, is dispersed in an aqueous medium in the form of macroscopic discrete particles and maintained in dispersion by agitation until polymerization is completed; thereupon stirring is stopped and the polymerization product is precipitated in the form of granules or globules. By the addition of small amounts of polymerization inhibitors to vinyl acetate polymerized in this manner, it has been found that the resultant product is in a more finely divided state than otherwise would be obtained.

In addition to hydroquinone and nitrobenzene, mentioned above, there are a number of other polymerization inhibitors which, when used in less than a polymerization-inhibiting amount, produce the advantageous action upon the polymerization process and products which have just been described. Among these agents may be mentioned salicylic acid, p-amino-phenol (Metol), hexadienal, phenol, cresol, resorcinol, pyrocatechol, pyrogallol, pyridine, quinoline, ani-

line, naphthylamine, p-nitroaniline, triethanolamine, diethylamine, hydrazine hydrate, benzaldehyde, acetophenone, tannin, urea, carbon disulfide, hydrogen sulfide and sulfur dioxide. The foregoing list of agents is not to be regarded as exhaustive, since I have found it to be a general rule that any agent which is capable of inhibiting polymerization in relatively substantial proportions is effective for producing the results of the present invention when used in proportions insufficient to substantially inhibit polymerization. It will be obvious to those skilled in the art that other compounds may be used for the same purpose and the suitability of any compound for the purpose may be easily determined by simple test.

The invention may be illustrated by the following examples:

Example I

A mixture of 100 cc. of vinyl acetate, 1.0 mg. of nitrobenzene and 0.36 gram of technical benzoyl peroxide was heated under a reflux condenser to a temperature of 70° C. The polymerization reaction, as manifested by vigorous boiling of the vinyl acetate, began after an induction period of about 11 minutes; after an additional period of 2½ hours the vinyl acetate was practically quantitatively polymerized to a solid block. The polymerization product, when dissolved as a 20% solution in ethyl acetate, had a viscosity of 40 seconds as measured by the Hercules Powder Company method. A 20% solution of the product in vinyl acetate had a viscosity of 50 seconds, as determined by the same method.

By the polymerization of vinyl acetate under the same conditions, but without the addition of nitrobenzene, the polymerization begins after an induction period of 15 to 20 minutes and requires four to five hours at a temperature of 74 to 76° to go to completion. The viscosity of a 20% solution of the product will range from about 100 to 150 seconds.

By increasing the amount of nitrobenzene utilized in the foregoing procedure from 1.0 to 2.5 mg., about 30 minutes is required for the polymerization to begin but it is completed after an additional period of only about 2¼ hours. A 20% ethyl acetate solution of the polymer thus obtained has a viscosity of 28 seconds while a corresponding vinyl acetate solution has a viscosity of 35 seconds.

By increasing the amount of nitrobenzene originally present to 15 mg., the polymerization begins at a temperature of 76° C., after an incubation period of 6 hours, but the polymerization is completed after an additional 3½ hours. A 20% solution of the polymer in ethyl acetate has a viscosity of 4.4 seconds and a 20% solution in vinyl acetate a viscosity of 5.5 seconds.

Example II

100 cc. of vinyl acetate containing 0.5 mg. of hydroquinone and 0.36 gram of benzoyl peroxide was polymerized in accordance with the procedure described in Example I at a temperature of 72° C. The polymerization initiated after a period of 15 minutes was complete after 4 hours. A 20% solution of the polymer in ethyl acetate had a viscosity of 244 seconds and a 20% solution in vinyl acetate had a viscosity of 305 seconds.

Example III

By carrying out Example I, but utilizing 0.5 mg. of hydrazine hydrate as the polymerization inhibitor, the induction period was 10 minutes

and the polymerization period 3½ hours. The polymerization product had a viscosity of 756 seconds in 20% ethyl acetate solution and 945 seconds in 20% vinyl acetate solution.

Example IV

Utilizing 0.5 mg. of diethylamine as the polymerization inhibitor in the process of Example I resulted in an induction period of 10 minutes, a polymerization period of 2½ hours and a viscosity of 10.5 seconds for a 20% ethyl acetate solution of the product and 13.1 seconds for 20% vinyl acetate solution of the product.

Example V

Utilizing 0.5 mg. of p-amino-phenol (Metol) as the polymerization inhibitor in the procedure of Example I, the induction period was 10 minutes, the polymerization period was 1½ hours and the viscosities of the product were 75.0 and 93.7 seconds for 20% ethyl acetate and vinyl acetate solutions, respectively.

Example VI

Utilizing 0.5 mg. of salicylic acid as the polymerization inhibitor in the process of Example I, the induction period was 5 minutes, the polymerization period was 3 hours and the viscosity of the product was 208 and 250 seconds in 20% ethyl acetate and vinyl acetate solution, respectively.

Example VII

Using 0.5 mg. of cresol as the polymerization inhibitor in the procedure of Example I, the incubation period was 20 minutes, the polymerization time 2½ hours and the viscosity of the product in 20% vinyl acetate solution about 1000 seconds.

Example VIII

Utilizing 0.5 mg. of pyrogallol as the polymerization inhibitor in the process of Example I, the induction period was 20 minutes, the duration of the polymerization reaction 3 hours, and viscosities of 20% solutions of the product in ethyl acetate and vinyl acetate, respectively, 382 and 478 seconds.

Example IX

Utilizing 0.5 mg. of acetophenone as the polymerization inhibitor in the process of Example I, the induction period was 15 minutes, the polymerization period was 3 hours and the viscosities of 20% solutions in ethyl acetate and vinyl acetate, respectively, were 817 and 1021 seconds.

Example X

Utilizing 0.5 mg. of hexadienal as the polymerization inhibitor in Example I, there was an induction period of 12 minutes, a polymerization period of 2 hours and the viscosities of the product were 900 and 1125 seconds for 20% solutions in ethyl acetate and vinyl acetate, respectively.

Upon increasing the amount of hexadienal to 2.5 mg., the induction period was 40 minutes, the polymerization period was 2½ hours and the viscosities of the product were 127.5 and 159.8 seconds for 20% ethyl acetate and vinyl acetate solutions, respectively.

With 5 mg. of hexadienal, the induction period was 45 minutes, the polymerization period was 2½ hours and the respective viscosities 33 seconds and 41.2 seconds.

By the addition of a combination of 0.5 mg. of hexadienal and 0.5 mg. of propionaldehyde the induction period was 15 minutes, the polymerization period was 2¼ hours and the viscosities of

the product were 2.0 seconds and 2.5 seconds, respectively, for 20% ethyl acetate and vinyl acetate solutions.

Example XI

The addition of 0.5 mg. of sulfur dioxide as the inhibitor in the procedure of Example I gave an induction period of 13 minutes, a polymerization period of 2½ hours and product viscosities of 11.4 seconds for 20% ethyl acetate solution and 14.2 seconds for a 20% vinyl acetate solution.

Example XII

The addition of 0.5 mg. of hydrogen sulfide as the polymerization inhibitor in the procedure of Example I gave an induction period of 5 minutes, a polymerization period of 2 hours and a product viscosity of 750 seconds for the 20% ethyl acetate solution and of 937 seconds for the 20% vinyl acetate solution.

Example XIII

Crude vinyl acetate to which had been added hydroquinone in the proportion of 20 grams per 100 kgs. of vinyl acetate was carefully fractionated, to produce a pure vinyl acetate. Two hundred and fifty kilograms of vinyl acetate thus obtained was emulsified in the cold in 400 kgs. of a 10% aqueous solution of a water-soluble partial acetate of polyvinyl alcohol (saponification number 120 to 130). To this emulsion was added 400 cc. of concentrated hydrogen peroxide solution and the emulsion then heated to a temperature of 60–61°C., whereupon polymerization began to take place. The reaction then proceeded without further heating. During a period of several hours an additional 550 kgs. of vinyl acetate and 510 kgs. of cold water were added to the reaction mixture. From time to time, whenever the reaction gave evidence of subsiding, further amounts of concentrated hydrogen peroxide solution were added, the total amount required being approximately 700 cc. As the reaction proceeded the temperature was allowed to rise until it reached approximately 85 to 90°C. at the conclusion of the polymerization. Practically quantitative conversion of the vinyl acetate to the polymer was secured after a period of approximately 8 hours. The polyvinyl acetate emulsion thus obtained had a viscosity of 127 seconds as measured by the Hercules Powder Company method. It had a settling number of 3.6, the settling number being an indication of the particle size and being determined by diluting 1 cc. of the emulsion with water to a volume of 100 cc. and measuring the amount of material settled out during a settling period of 90 minutes.

By carrying out the foregoing procedure without adding hydroquinone to the crude vinyl acetate prior to fractionation, the polymerization was completed in 7 hours and the emulsion had a viscosity of only 45 seconds. The settling number was 10, indicating that the emulsified particles were considerably larger in size than those obtained with vinyl acetate containing hydroquinone.

By repeating the foregoing procedure, with the exception that crude vinyl acetate containing 10 grams of hydroquinone per 100 kgs. of crude

vinyl acetate was subjected to steam distillation prior to polymerization, the polymerization under the same conditions took place in 9 hours and a polyvinyl acetate emulsion having a viscosity of 470 seconds and a settling number of 2.5 was obtained. In this case the distilled vinyl acetate contained a larger percentage of hydroquinone due to the fact that the latter was partially volatilized during the steam distillation.

Starting with 800 kg. of pure vinyl acetate containing 10 grams of hydroquinone, polymerization under the conditions described above was completed after 15 hours and a polyvinyl acetate emulsion with a settling number of 1.1 and a viscosity exceeding 1000 seconds was obtained. The emulsion was of a pasty consistency and its viscosity could be increased even further by the addition of plasticizers. Even upon reducing the hydroquinone content to as low as 5 grams per 800 kgs. of pure vinyl acetate it is still possible to obtain pastes or emulsions of any desired consistency in which the particle size is exceedingly small and which are of excellent stability.

As indicated by the foregoing examples, by suitable selection of the polymerization inhibitor and the quantity used, it is possible to vary the degree of polymerization within wide limits. Furthermore, the particle size of the polymer emulsions can be reduced to a surprising extent and at the same time a considerable saving in the amount of emulsifying agent used be effected.

It is to be noted that all polymerization inhibitors do not function in precisely the same manner; accordingly, the selection of the particular inhibitor will depend upon the results desired in each case. For example, salicylic acid and p-amino-phenol are particularly useful in accelerating the rate of polymerization; other inhibitors such as, for example, cresol and hexadienal, function primarily to increase the viscosity of polymer emulsions. In case of hexadienal, as is indicated by Example X, it is possible to regulate the degree of polymerization of the product over an exceedingly wide range by suitably adjusting the proportion of hexadienal added. It is advantageous in certain instances to combine two or more polymerization inhibitors in order to obtain a desired combination of properties in the polymerized product.

It may be noted that the polymerization inhibitors of the present invention may be utilized in polymerization inhibiting amounts for stabilizing monomeric vinyl acetate while in storage. When it is desired to subject the stabilized monomer to polymerization, it may be distilled under carefully controlled conditions so that the inhibitor is incompletely removed and only that amount which is required for the desired modification of the polymerization process will remain.

It is to be understood that the invention is not restricted to the specific illustrative embodiments thereof described hereinabove, but includes all such variations, modifications and equivalents as fall within the scope of the appended claims.

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