

UNITED STATES PATENT OFFICE

2,294,226

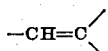
PREPARATION OF GRANULATED POLYMERS AND COPOLYMERS

Gaetano F. D'Alelio, Pittsfield, Mass., assignor to General Electric Company, a corporation of New York

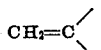
No Drawing. Application October 28, 1939, Serial No. 301,812

14 Claims. (Cl. 260—32)

This invention relates to the art of granulating hardenable organic materials. More particularly the invention is concerned with certain improvements and modifications in converting single or mixed polymerizable solidifiable organic compounds containing the structure



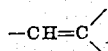
for example single or mixed monomeric or partially polymerized, hardenable organic compounds containing at least one



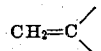
grouping, more particularly polymerizable, hardenable aliphatic esters, into granular polymers or copolymers. This application is a continuation-in-part of my copending application Serial No. 294,498, filed September 12, 1939, and assigned to the same assignee as the present invention.

In the technical utilization of thermoplastic molding materials comprising thermoplastic polymerized organic substances it is economically desirable to have the polymerized body in a finely divided state. While this may be accomplished by the mechanical disruption of large pieces of polymeric masses, or by solvent precipitation technique, such methods are not completely satisfactory. The former requires equipment capable of withstanding high mechanical stresses and is time-consuming and expensive, while the latter requires the use of expensive solvent-recovery systems to render the process economically feasible. The most satisfactory method comprises initially obtaining the thermoplastic material in the desired granular form.

I have discovered that soluble polymerized unsaturated polycarboxylic compounds selected from the class consisting of soluble polymeric unsaturated alpha beta polycarboxylic acids, soluble salts thereof and mixtures of such acids and salts comprise effective granulating agents for converting masses of non-granular, hardenable, polymerizable organic compounds, more particularly single or mixed, flowable, monomeric or partially polymerized, solidifiable organic compounds containing the structure

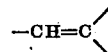


specifically a



grouping, from liquid or semi-solid state to solid,

granular, polymeric modifications capable of direct technical utilization. Examples of soluble, polymerized, unsaturated polycarboxylic compounds which may be used in carrying the present invention into effect are soluble, polymeric acids such as itaconic, fumaric, maleic, mesaconic, citraconic, aconitic, etc., soluble salts of such acids, for example the water-soluble salts such as the alkali-metal (sodium, potassium, lithium, caesium and rubidium) and the ammonium salts thereof, and mixtures of such acids and salts. Examples of polymerizable, hardenable organic compounds, more particularly solidifiable, polymerizable organic compounds containing a



grouping, specifically a



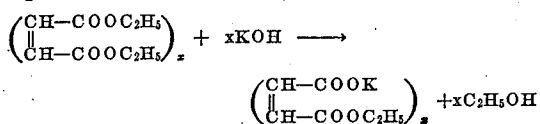
grouping, which may be converted into granular polymers or copolymers with the aid of the above-defined polymerized unsaturated polycarboxylic compounds are polymerizable esters such, for instance, as polymerizable methyl methacrylate, ethyl methacrylate, methyl acrylate, dimethyl itaconate, etc., and mixtures of two or more such polymerizable esters.

In producing the granular polymers or copolymers in accordance with this invention a polymerization catalyst, for instance an oxygen-liberating catalyst such as a super-oxide (examples of which are peroxides of the aromatic acid series, e. g. benzoyl peroxide, etc., aliphatic acyl peroxides, e. g. acetyl peroxide, stearyl peroxide, etc.) preferably is incorporated into the material to be granulated. The polymerizable body containing the polymerization catalyst is dispersed, as by rapid stirring, in the dispersion medium (for example water) containing the polymerized unsaturated polycarboxylic compound in solution state. The polymerizable organic compound is caused to be polymerized while maintaining it in a dispersed state in the dispersion medium. The solid granules of polymeric material which form are separated from the dispersion medium by suitable means. The invention is particularly adapted for the production of granular copolymers, yielding homogeneous copolymers even from those polymerizable compounds having widely different rates of polymerization. This was quite surprising and unexpected.

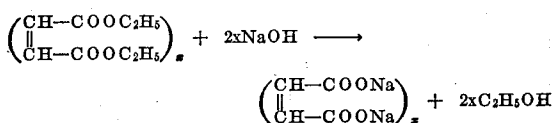
I have further discovered that the polymeric unsaturated polycarboxylic compounds of this invention are best obtained and have greatest util-

ity as granulating agents when produced by the hydrolysis of polymerized esters, advantageously alkyl esters, of unsaturated alpha beta polycarboxylic acids. I have found that I can obtain a higher molecular weight polymerized unsaturated alpha beta polycarboxylic acid by an alkaline or an acid hydrolysis of the polymerized alkyl (methyl, ethyl, propyl, butyl, etc.) esters of the polycarboxylic acid than is possible through a direct polymerization of the acid itself. Granulating agents comprising the polymerized water-soluble salts of the unsaturated alpha beta polycarboxylic acids also are of higher molecular weight when derived from a polymerized ester of the acid than when prepared by direct polymerization of a salt of the acid or by forming a salt of the directly polymerized acid. Granulating agents prepared by any of these methods may be used in forming granular polymers and copolymers, but those derived from the polymerized esters have a higher granulating efficiency and therefore are preferred.

A further advantage obtained by using the preferred granulating agents of this invention in forming granular polymers and copolymers is that the granulating effect, for example the particle size and general appearance of the finished product, can be considerably varied, as desired or as conditions may require (and when other factors are the same), by varying the extent of hydrolysis of the polymerized ester. Thus, taking polymeric diethyl maleate as an example, I may treat the ester with sufficient alcoholic potassium hydroxide to form a polymeric half ester salt or, by using 2 mols alkali (e. g., sodium hydroxide), the polymeric disodium maleate, as illustrated by the following equations:



and



The free polymeric acids may be obtained by treating the polymeric mono- or di-salts with inorganic acids such as sulfuric, hydrochloric, phosphoric, etc. The free polymeric acids also may be prepared by treating the polymeric mono- or di-ester with inorganic acids in the presence of water. The degree of hydrolysis depends, for example, upon the mol ratio of the salt-forming compound (alkali, etc.) to the polymerized ester, or upon the amount of water and inorganic acid available during hydrolysis.

The highly polymerized unsaturated alpha beta polycarboxylic acids as thus prepared by hydrolysis of polymerized esters of the acids, or the polymerized soluble salts of these acids may be purified, if desired, for example by reprecipitation from suitable solvents such as alcohol, acetone, dioxane, etc. Many of these polymerized salts of unsaturated alpha beta polycarboxylic acids are believed to be new chemical compounds.

In order that those skilled in the art better may understand how the present invention may be carried into effect, the following illustrative examples of the preparation of these new granu-

lating agents and of their utilization in the production of granular polymers and copolymers are given. All parts are by weight.

PREPARATION OF GRANULATING AGENTS

Example 1

	Parts
Polymerized dimethyl itaconate (finely ground)	19.8
Potassium hydroxide	7.01
Ethyl alcohol (95%)	160.0

The potassium hydroxide was dissolved in the ethyl alcohol, the polymerized itaconate was added slowly thereto with rapid stirring and the whole heated and stirred under reflux for 5 hours, at the end of which time a fine powdery material (potassium methyl polyitaconate) had formed. It was removed from the alcoholic solution by filtration and dried. This mono-potassium salt was completely soluble in water in contrast with the water-insoluble nickel, aluminum, barium, ferric, lead, silver and mercuric salts which also were prepared. Treatment of the potassium methyl polyitaconate (polymerized potassium methyl ester of itaconic acid) with an equal molar quantity of hydrogen chloride yielded a mono-methyl ester of polyitaconic acid which was insoluble in water but soluble in alcohol (95%) and in dilute sodium hydroxide solutions.

Example 2

	Parts
Polymerized dimethyl itaconate (finely ground)	12.0
Potassium hydroxide	8.6
Ethyl alcohol (95%)	160.0
Water	50.0

The above components were heated and stirred under reflux for 6 hours, first forming a solution of the potassium hydroxide as described under Example 1 before adding the polymerized itaconate thereto and refluxing the whole. A reaction product comprising the dipotassium salt of polymerized itaconic acid was obtained by evaporation of the solvent and washing with alcohol to purify the salt. The polyitaconic acid obtained by treating this di-salt with inorganic acids was insoluble in water but readily soluble in dilute alkali solutions.

Example 3

	Parts
Polymerized dimethyl fumarate	17.2
Potassium hydroxide	14.0
Ethyl alcohol	160.0

were treated in a manner similar to that described under Examples 1 and 2. The dipotassium polyfumarate thus obtained was soluble in water. Polymeric fumaric acid, insoluble in water, was prepared by acidifying an aqueous solution of the di-salt with mineral acids.

Example 4

	Parts
Polymerized dimethyl fumarate	20
Sulfuric acid (approximately 98%)	4
Water	80

were refluxed with stirring for 24 hours. The sulfuric acid was neutralized with the calculated amount of a 10% aqueous sodium hydroxide solution. The mixture was dried at 100° C. to remove water and then purified by extraction with ethyl alcohol, yielding a hydrolyzed polyfumaric ester that was soluble in water.

UTILIZATION OF GRANULATING AGENTS

Example 5

	Parts
Monomeric methyl methacrylate.....	25.0
Benzoyl peroxide (dissolved in the above) ..	0.25
Water.....	90.0
Mono-potassium methyl polyitaconate of Example 1.....	0.25

were mixed and heated at 85° C. for 3 hours with stirring. Beads of polymerized methyl methacrylate about 1 to 2 mm. in diameter were filtered from the aqueous vehicle and dried for 3 hours at 55° C. These beads or granules were easily molded at 140° C. under a pressure of 4000 pounds per square inch for 5 minutes, yielding clear, hard molded articles of good surface appearance.

Example 6

	Parts
Monomeric methyl methacrylate.....	25.0
Benzoyl peroxide (dissolved in the above) ..	0.25
Water.....	100.0
Dipotassium polyitaconate of Example 2.....	0.25

were treated in essentially the same manner as described under Example 5 to obtain white, polymeric, non-spherical granules of irregular shape. The molded articles were similar in appearance and molding characteristics to those made from the granules of Example 5.

Example 7

	Parts
Monomeric ethyl methacrylates.....	20.0
Monomeric dimethyl itaconate.....	10.0
Benzoyl peroxide (dissolved in the above) ..	0.3
Water.....	130.0
Polymerized itaconic acid * in an aqueous alkaline solution of 0.3 part sodium hydroxide in 10 parts water.....	0.3

*NOTE.—The polymerized itaconic acid was derived from the dipotassium polyitaconate of Example 2 by acidification of the latter with sulfuric acid.

The above components were treated in essentially the same manner as described under Example 5 with the exception that heating was carried out at a temperature of 90° to 100° C. Twenty-five (25) parts of very fine beads of ethyl methacrylate-dimethyl itaconate copolymer were obtained. These beads were dried and then molded at approximately 140° C. under a pressure of about 4000 pounds per square inch. The molded articles were clear, hard and of good surface finish.

Example 8

	Parts
Monomeric ethyl methacrylate.....	21.0
Monomeric dimethyl itaconate.....	9.0
Monomeric diallyl itaconate.....	0.3
Benzoyl peroxide (dissolved in the above) ..	0.6
Water.....	150.0
Disodium polyitaconate (polymerized disodium itaconate).....	0.3

were mixed and the polymerizable materials copolymerized by heating the mixture at 85° to 90° C. for two hours with stirring. Twenty-five (25) parts of small, clear, colorless beads or granules of the copolymer were obtained by filtration of the above solution at the end of the polymerization period. Clear, hard, molded articles were produced by molding the dried beads at suitable elevated temperatures and

pressures, for example at 130° to 150° C. and at pressures of the order of 4000 to 6000 pounds per square inch.

Example 9

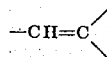
Same formula and essentially the same technique were followed in making granular copolymers and molded articles therefrom as described under Example 8 with the exception that the granulating agent comprised 0.3 part of polymerized itaconic acid in an aqueous alkaline solution of 0.3 part sodium hydroxide in 10 parts water. The polymerized itaconic acid was obtained by acidifying the polymerized dipotassium itaconate (dipotassium polyitaconate) of Example 2 with sulfuric acid and thereafter washing the mass with a suitable solvent to remove excess acid and sodium sulfate. The ethyl methacrylate-dimethyl itaconate-diallyl itaconate interpolymer was obtained in the form of glass-clear granules.

Example 10

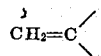
	Parts
Monomeric ethyl methacrylate.....	17.0
Monomeric dimethyl itaconate.....	13.0
Benzoyl peroxide (dissolved in the above) ..	0.3
Water.....	130.0
Dipotassium polyfumarate (polymerized dipotassium fumarate) of Example 3.....	0.3

were mixed and the polymerizable materials copolymerized by heating and stirring for 5 hours at 85° to 90° C. Glass-clear beads having a diameter of the order of 1 to 2 mm. were obtained. From these beads or granules clear, colorless molded articles were obtained by molding at approximately 140° C. for 5 minutes at pressures of the order of 5000 to 6000 pounds per square inch.

From the foregoing it will be seen that the granulating agents of this invention have a protective action on a system comprising a dispersed phase of a polymerizable, hardenable organic compound containing the structure



more particularly polymerizable, hardenable organic compounds having at least one



grouping, in a dispersion medium in which the granulating agent is soluble and the polymerizable organic compound is substantially insoluble. Water is an example of a suitable dispersion medium in which the polymerizable organic compound advantageously may be dispersed. Water is preferred as the dispersion medium for obvious economic reasons, although it will be apparent to those skilled in the art that numerous other dispersion mediums may be employed, the choice depending upon the initial cost and the solubility of the granulating agent and the insolubility of the polymerizable and the polymerized organic compound therein. The action of these granulating agents in increasing the stability of the dispersed organic compound until solid polymers are formed appears to be analogous to that of an emulsifying agent in protecting an emulsion.

The size and shape of the granulated polymerized organic compound depends, for example, upon such influencing variables as the concentration of the granulating agent, the concentration

of the dispersion medium, the purity of the granulating agent, the speed of stirring, the solubility and other characteristics of the polymerizable and the polymerized organic compound, the pH of the mixture, whether the polymerized body is a homogeneous compound (a polymer) or a heterogeneous compound (a copolymer), and the solubility in the dispersion medium and the other characteristics of the particular granulating agent employed.

The granules of the polymerized organic compound may be separated from the dispersion medium by filtration, centrifuging, etc., and further dried, if necessary, by suitable means. The dried granules may be molded directly or they may be sheeted first and then molded. They also may be dissolved in suitable solvents and the resulting liquid compositions used as surface coating materials. The dried beads also may be used to surface a base member. In such applications they serve as focal points for light reflection. Sheet materials such as paper, cloth, etc., when faced on one or both sides with the resin granules likewise may be compressed under heat sufficient to cause the resin to flow and to form a smooth or embossed surface finish.

The granulating agent may be recovered from the dispersion medium and may be re-used. Or, the dispersion medium (e. g., a dispersion medium comprising water) containing the granulating agent may be recovered and re-used, adding if necessary, additional granulating agent to the recovered solution to provide a dispersion medium containing the desired concentration of granulating agent.

It will be apparent to those skilled in the art that this invention is not limited to the granulation of the particular organic materials mentioned in the above illustrative examples and that numerous other polymerizable, hardenable organic compounds similarly may be granulated. Additional examples of compounds that may be granulated with the aid of the granulating agents herein described are monomeric or partially polymerized diethyl itaconate, diallyl itaconate, ethyl acrylate, methyl ethacrylate, vinyl compounds such as vinyl acetate, etc., and mixtures of these and other polymerizable organic compounds such, for example, as mixtures of polymerizable diethyl itaconate and methyl methacrylate, vinyl acetate and methyl methacrylate, ethyl acrylate and ethyl methacrylate, methyl acrylate and glycol dimethacrylate, styrene and propyl methacrylate, etc. In general, any normally flowable, hardenable, polymerizable organic compound containing a $-\text{CH}=\text{C}-$ grouping, specifically a $\text{CH}_2=\text{C}-$ grouping, that is capable of being dispersed in a dispersion medium in which the granulating agents of this invention are wholly or partly soluble, and which in the chosen medium can be polymerized (with or without a polymerization catalyst) to a solid state, can be converted into solid granules of varying particle size and shape with the aid of these new granulating agents.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of converting a polymerizable, hardenable mass comprising a polymerizable, hardenable aliphatic ester into a granular polymeric modification which comprises dispersing said mass in a dispersion medium comprising water in which the said mass is insoluble, said dispersion medium containing a granulating agent soluble therein, said agent comprising a soluble polymerized unsaturated polycarboxylic

compound selected from the class consisting of soluble polymeric unsaturated alpha beta polycarboxylic acids, soluble salts thereof, and mixtures of such acids and salts, and causing the said polymerizable mass to be polymerized while maintaining the same in a dispersed state in the said dispersion medium.

2. The method of converting a polymerizable, hardenable mass comprising a polymerizable, hardenable aliphatic ester into a granulated polymeric modification which comprises incorporating into the said mass a polymerization catalyst, dispersing the resulting mass in a dispersion medium comprising water containing a water-soluble salt of a polymeric unsaturated alpha beta polycarboxylic acid, polymerizing the said mass, and maintaining the said polymerizable mass in a dispersed state in the said dispersion medium during polymerization.

3. A method as in claim 1 wherein the granulating agent comprises an alkali-metal salt of a polymeric unsaturated alpha beta polycarboxylic acid.

4. A method as in claim 1 wherein the granulating agent comprises a polymerized alkali-metal salt of itaconic acid.

5. A method as in claim 2 wherein the water-soluble salt of a polymeric unsaturated alpha beta polycarboxylic acid is a water-soluble salt of polymeric itaconic acid.

6. The method of converting a polymerizable, hardenable mass comprising an ester of methacrylic acid into a granulated polymeric modification which comprises dispersing the said mass in a dispersion medium comprising water containing a water-soluble salt of a polymeric unsaturated alpha beta polycarboxylic acid, polymerizing the said mass, and maintaining the said mass in a dispersed state in the said dispersion medium during polymerization.

7. A method as in claim 6 wherein the ester of methacrylic acid is methyl methacrylate.

8. A method as in claim 1 wherein the granulating agent comprises a polymerized alkali-metal salt of maleic acid.

9. A method as in claim 1 wherein the granulating agent comprises a polymerized alkali-metal salt of fumaric acid.

10. A method as in claim 2 wherein water-soluble salt of a polymeric unsaturated alpha beta polycarboxylic acid is a water-soluble salt of polymeric maleic acid.

11. A method as in claim 2 wherein the water-soluble salt of a polymeric unsaturated alpha beta polycarboxylic acid is a water-soluble salt of a polymeric fumaric acid.

12. The method of converting a polymerizable, hardenable mass comprising an ester of acrylic acid into a granulated polymeric modification which comprises dispersing the said mass in a dispersion medium comprising water containing a water-soluble salt of a polymeric unsaturated alpha beta polycarboxylic acid, polymerizing the said mass, and maintaining the said mass in a dispersed state in the said dispersion medium during polymerization.

13. The method of converting a polymerizable, hardenable mass comprising a vinyl ester into a granulated polymeric modification which comprises dispersing the said mass in a dispersion medium comprising water containing a water-soluble salt of a polymeric unsaturated alpha beta polycarboxylic acid, polymerizing the said mass, and maintaining the said mass in a dis-

persed state in the said dispersion medium during polymerization.

14. The method of converting a polymerizable, hardenable mass comprising vinyl acetate into a granular polymeric modification which comprises incorporating into the said mass a peroxide polymerization catalyst, dispersing the resulting mass in a dispersion medium comprising water

containing a polymerized alkali-metal salt of an unsaturated alpha beta polycarboxylic acid, polymerizing the said mass, and maintaining the said polymerizable mass in a dispersed state in the said dispersion medium during polymerization.

GAETANO F. D'ALELIO.