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PROCESS FOR THE PREPARATION OF SOLUBLE POLYMERS OF UNSATURATED ESTERS OF POLYCARBOXYLIC ACIDS

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5 Claims. (Cl. 260—78.4)

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This invention relates to the polymerization of polymerizable unsaturated compounds.

Many unsaturated organic compounds can be polymerized to valuable resins useful in the production of coatings, impregnants, laminates, cast shapes and the like. In many cases, particularly in the production of coatings, it is difficult to polymerize the material without forming imperfections such as pock marks and pin holes which mar the appearance and impair the physical properties of the products.

An object of the present invention is to provide a new and improved method of polymerizing unsaturated compounds. Another object is to provide for the production of new compositions comprising partial polymers of polymerizable unsaturated organic compounds. Another object is to provide compositions adapted for the production of improved coatings and the like from polymerizable unsaturated compounds. Other objects will be apparent from the description of the invention given hereinafter.

These objects are accomplished in accordance with the present invention by the polymerization of partially polymerized polyfunctional unsaturated compounds in solution in an inert solvent in the substantial absence of unreacted polymerizable monomer. The resulting solutions can be employed in the presence or absence of additional solvent or non-solvent diluent in the production of improved coatings, laminates, etc.

One procedure by which the improved products can be obtained comprises partially polymerizing a polyfunctional unsaturated compound, removing unreacted monomer, subsequently further but incompletely polymerizing the substantially monomer-free partial polymer in the presence of an inert volatile solvent and finally substantially completing the polymerization with the volatilization of the solvent. By the use of this procedure coatings and the like can be produced substantially free from imperfections. Comparable products have not been obtained in any other way.

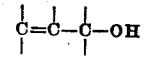
The term "polyfunctional, unsaturated compound" as used herein designates compounds having in the molecule two or more polymerizable unsaturated carbon-to-carbon linkages. The most important compounds for the purposes of the present invention have at least two unsaturated carbon-to-carbon linkages unconjugated with respect to carbon. Of these a subgroup consists of unsaturated aliphatic organic polyesters of polyhydric alcohols such as the acrylic, methacrylic and crotonic polyesters of

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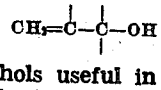
glycol, diethylene glycol, glycerol, polyvinyl alcohols, polyallyl alcohols and the like. Another subgroup consists of unsaturated aliphatic esters of unsaturated aliphatic monocarboxylic acids such as vinyl, allyl and methallyl esters of acrylic, methacrylic, chloroacrylic, crontonic and cinnamic acids. Others are unsaturated esters of inorganic acids such as the vinyl, allyl and methallyl esters of phosphoric, orthosilicic and orthoboric acids. A preferred subgroup, which consists of those compounds with which the importance of the invention is most apparent, comprises esters of polycarboxylic acids with unsaturated alcohols of aliphatic character.

Suitable unsaturated alcohols whose radicals may constitute a part of the compounds with which the invention is particularly concerned are those having an unsaturated linkage of aliphatic character between two carbon atoms, one of which is attached directly to a carbon atom, which in turn is attached directly to an alcoholic hydroxyl group. These compounds are alcohols of aliphatic character having an unsaturated linkage between two carbon atoms, at least one of which is not more than once removed from an alcoholic hydroxyl group.

One subgroup of unsaturated alcohols within the foregoing definition consists of allyl-type alcohols. Allyl-type alcohols are unsaturated alcohols having a double bond of aliphatic character between two carbon atoms, one of which is joined directly to a saturated carbinol carbon atom. They have a structure which may be represented by the general structural formula



Preferred allyl-type alcohols have a terminal methylene group attached directly by an olefinic double bond to a carbon atom which in turn is attached directly to a saturated carbinol carbon atom, as represented by the formula



Allyl-type alcohols useful in the present invention preferably have not more than about eighteen carbon atoms and have at least one unsaturated carbon-to-carbon linkage for each six carbon atoms.

Representative examples of preferred allyl-type alcohols are the following: allyl alcohol, methallyl alcohol, ethallyl alcohol, chloroallyl alcohol, buten-1-ol-3, penten-1-ol-3, hexen-1-ol-3, 3-methyl-buten-1-ol-3, 3-methyl-penten-1-ol-3,

2-methyl-buten-1-ol-3, 2-methyl-penten-1-ol-3, 2,3-dimethyl-buten-1-ol-3, hepten-1-ol-3, 4-methyl-hexen-1-ol-3, 5-methyl-hexen-1-ol-3, 4,4'-dimethyl-penten-1-ol-3, octen-1-ol-3, 6-methyl-hepten-1-ol-3, 4-methyl-hepten-1-ol-3, 4,4'-dimethyl-hexen-1-ol-3, 3-phenyl-propen-1-ol-3, 3-tolyl-propen-1-ol-3, 3-xylyl-propen-1-ol-3, 4-phenyl-buten-1-ol-3, 4-tolyl-buten-1-ol-3, 4-xylyl-buten-1-ol-3, 3-naphthyl-propen-1-ol-3, 4-chloro-buten-1-ol-3, pentadien-1,4-ol-3, hexen-1-yn-5-ol-3, 2-methyl-penten-1-yn-4-ol-3, and 2,5-dimethyl-hexadien-1,5-ol-4. Other allyl-type alcohols are crotyl alcohol, tiglyl alcohol, 3-chloro-buten-2-ol-1, cinnamyl alcohol, hexadien-2,4-ol-1, hexadien-2,5-ol-1, butadien-2,3-ol-1, hexadien-3,5-ol-2, 2-methyl-hexen-2-ol-1, 2-methyl-penten-2-ol-1, 3,7-dimethyl-octadien-2,7-ol-1, cyclopenten-2-ol-1, cyclohexen-2-ol-1, etc.

Another subgroup of suitable unsaturated alcohols consists of alpha-unsaturated aliphatic alcohols, e. g. vinyl-type alcohols, which are compounds having a double bond of aliphatic character between two carbon atoms, one of which is attached directly to an alcoholic hydroxyl group, as represented by the general formula

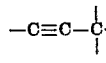


Of the vinyl-type alcohols a preferred subgroup consists of compounds having a terminal methylene group attached directly by an olefinic double bond to a carbinol carbon atom, as represented by the general formula



Examples of preferred vinyl-type alcohols are vinyl alcohol, isopropenol, buten-1-ol-2, etc. Examples of other vinyl-type alcohols are propen-1-ol-1, buten-1-ol-1, cyclohexen-1-ol-1, cyclopenten-1-ol-1, etc. Vinyl alcohol is the preferred specific alpha-unsaturated alcohol.

Other unsaturated alcohols whose radicals may constitute part of the compounds with which the invention is concerned are those having a triple bond of aliphatic character between two carbon atoms, one of which is attached directly to a saturated carbon atom, which in turn is attached directly to an alcoholic hydroxyl group, as represented by the general formula



as exemplified by propargyl alcohol, pentyn-3-ol-2,2-methyl-hexyn-3-ol-2.

Polycarboxylic acids whose radicals may form part of the preferred esters in accordance with the invention include saturated aliphatic acids such as oxalic, malonic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, tartaric, citric, tricarballylic, etc. Another group consists of ethereal oxygen-containing polycarboxylic acids such as diglycolic, dilactic, dihydracrylic, etc. Another group consists of sulfonyl-containing polycarboxylic acids, e. g. sulfonyl diglycolate, sulfonyl dihydracrylate, sulfonyl dilactate, etc. Another group consists of unsaturated aliphatic polycarboxylic acids such as itaconic, citraconic, aconitic, etc. Another and preferred group consists of aromatic polycarboxylic acids, i. e. acids having two or more carboxyl groups attached directly to an aromatic ring. Among the many suitable aromatic polycarboxylic acids are phthalic, isophthalic, terephthalic, naphthalene dicarboxylic, dimethyl phthalic, dichlorophthalic, etc. acids and the corresponding higher polycarboxylic acids. Among the many other suitable acids are tetrachlorophthalic acid and the other polyhalobenzene polycarboxylic acids.

Simple or mixed esters may be used.

Examples of suitable polymerizable unsaturated aromatic polycarboxylic acid esters are diallyl phthalate, dimethallyl phthalate, dichloroallyl phthalate, diethallyl phthalate, diallyl isophthalate, dimethallyl isophthalate, allyl chloroallyl phthalate, allyl crotyl phthalate, diallyl tetrachlorophthalate, dimethallyl tetrachlorophthalate, divinyl phthalate, di-isopropenyl phthalate, allyl vinyl phthalate, methallyl vinyl phthalate, chloroallyl vinyl phthalate, allyl isopropenyl phthalate, methallyl isopropenyl phthalate, allyl (butene-1-yl-2) phthalate, crotyl vinyl phthalate, crotyl propargyl phthalate, allyl propargyl phthalate and the corresponding esters of the higher polycarboxylic aromatic acids. The compound specifically preferred by reason of its stability under polymerization conditions, the ease and comparative cheapness of its preparation, its ready polymerizability and the high quality and reproducibility of products containing the polymer is diallyl phthalate.

Examples of suitable unsaturated esters of saturated aliphatic acids are diallyl oxalate, divinyl oxalate, diallyl malonate, diallyl adipate, allyl vinyl adipate, diallyl citrate, triallyl citrate, etc. Examples of suitable unsaturated esters of ethereal oxygen-containing polycarboxylic acids are diallyl diglycolate, diallyl dihydracrylate, diallyl dilactate, dimethallyl diglycolate, allyl vinyl diglycolate, etc. Examples of suitable esters of sulfonyl-containing carboxylic acids are diallyl sulfonyl diglycolate (also known as diallyl dimethyl sulfone alpha,alpha'-dicarboxylate), diallyl sulfonyl dihydracrylate (also known as diallyl diethyl sulfone beta,beta'-dicarboxylate), etc. Examples of unsaturated aliphatic polycarboxylic acid esters which may be polymerized in accordance with the invention are diallyl itaconate, diallyl citraconate, etc.

As the polymerization of a polymerizable unsaturated compound progresses the percentage of monomer decreases and the percentage of polymer increases. An increase in polymer content is accompanied by an increase in refractive index and in viscosity. In the case of compounds containing in the molecule two or more polymerizable unsaturated carbon-to-carbon linkages unconjugated with respect to carbon, the polymer first formed is fusible and soluble in many common organic solvents. The structure of the molecule in this stage is presumably substantially linear. The polymer in this stage is soluble in the corresponding monomer and usually is soluble also in the monomer of other polymerizable unsaturated compounds. It can usually be separated from its solution with monomer by precipitation with selected liquids or by fractional distillation. As the polymerization of such a compound progresses, cross-linking increases and more and more of the polymer has a cross-linked or three-dimensional structure as distinguished from the earlier produced linear structure. As cross-linking increases the general solubility of the polymer decreases and the monomer/polymer mixture may become a gel. Continued polymerization converts more of the residual monomer to polymer and also further increases cross-linking, further reducing solubility and fusibility, i. e. capability of being ren-

dered plastic by heat without substantial decomposition or degradation. Eventually substantially all of the material is converted to a condition of infusibility and insolubility in most common solvents.

The first step of procedure in accordance with the invention comprises producing a solution of a monomer and polymer. This may be accomplished by partially polymerizing the ester to below the point of gel formation under the particular conditions involved. It is preferred to polymerize in bulk, i. e. in the absence of added solvents or other diluents. However, if desired, the ester may be polymerized in solution, emulsion or impermanent suspension. The polymerization is preferably effected at elevated temperatures in the absence of added polymerization catalyst. Polymer produced by polymerization at elevated temperatures in the absence of added polymerization catalyst is herein termed "thermal polymer." For the non-catalytic polymerization of diallyl phthalate and related compounds, temperatures of from about 50° C. to about 250° C. or even higher may be used, the more narrow range of from about 200° C. to about 225° C. being preferred. When the polymerization is conducted in the presence of a polymerization catalyst of the type most generally used, e. g. a peroxide, such as benzoyl peroxide, lower temperatures are feasible, the range of from about 50° C. to about 100° C. being preferred. Amounts of catalyst as small as 0.1% or less of benzoyl peroxide or equivalent, are effective. Larger amounts, e. g. 5% or more of benzoyl peroxide or equivalent, can be used.

As polymerization progresses the refractive index of the monomer-polymer mixture increases. For practical purposes the refractive index can be used as a reasonably accurate indication of polymer content, at least up to gel formation in the case of compounds having two or more unsaturated unconjugated linkages in the molecule. A convenient procedure consists in experimentally determining the refractive index at the gel point, i. e. the point at which a gel begins to be produced, under the desired conditions of polymerization, and, thereafter, arresting polymerization at a lower refractive index. A substantial margin of safety is desirably provided, the refractive index (n 20/D) at the point of interruption of polymerization being from about 0.0020 to about 0.0075 less than the refractive index at the gel point.

If desired, of course, other methods can be used for following polymerization and determining the point of interruption. Viscosity is a function of polymerization and may be used as a measure. Gravimetric methods are satisfactory.

The second step of procedure in accordance with the invention comprises separating unreacted monomer from polymer. This can be accomplished by mixing the monomer/polymer solution with a sufficient amount of a liquid which is a solvent for the monomer but a non-solvent for the polymer to preciptate the polymer, precipitation being followed by centrifugation, filtration or the like. Another method comprises removing unreacted monomer by distillation, preferably under reduced pressure. The removal can be facilitated by the use of non-reactive liquid forming an azeotropic mixture with a monomer, by sweeping with an inert gas, such as nitrogen or carbon dioxide, or by other known or special methods. Separation by distillation is

particularly desirable in the case of monomer/polymer solutions produced by polymerization in the absence of catalyst. If desired, polymerization inhibitors may be used to prevent undesired polymerization during distillation. Other methods of separation may be used.

The third step of procedure in accordance with the invention comprises further polymerizing the partial polymer obtained by the first and second steps in the absence of a polymerizable unsaturated monomer, but in solution in an inert solvent. Organic solvents are preferred. Examples of suitable organic solvents for polymeric diallyl phthalate and related compounds produced by bulk polymerization to below the gel point in the absence of added polymerization catalyst are carbitol, isophorone, acetone, methyl ethyl ketone, toluene, xylene, benzene, cyclohexanone, dichloroethyl ether, chloroform, methyl carbitol, methyl cellosolve, cellosolve acetate, acetonyl acetone, and mixtures of these with one another and with other suitable substances. There are, of course, large numbers of suitable solvents other than those listed above. The ratio of polymer to solvent may be varied over a wide range. It is preferred to use at least about 25 parts of solvent per 100 parts of polymer by weight, more preferably from about 75 to about 125 parts of solvent per 100 parts of polymer by weight are employed. However, if desired, much larger amounts of solvent may be used, e. g. 100 parts of solvent per part of polymer by weight.

It has been found that polymers produced by the bulk polymerization of an unsaturated polyester of an aromatic polycarboxylic acid, e. g. diallyl phthalate, to just below the gel point can in the absence of monomer be caused to undergo substantial further polymerization in solution in an inert organic solvent without gelling. The polymerization is accompanied by a continuous increase in viscosity and refractive index, either or both of which can be used to follow the course of the reaction and to determine the optimum point at which the reaction should be arrested. As in the case of the first step of procedure in accordance with the invention, it is in general preferred to stop the reaction short of the point at which gel formation occurs, e. g. at a refractive index (n 20/D) from about 0.0020 to about 0.0075 less than the refractive index at the gel point under the particular conditions involved. On the basis of viscosity it is preferred to polymerize sufficiently to increase the viscosity of the polymer solvent mixture by an amount at least equal to the interval B to V on the Gardner-Holdt scale, the amount of solvent remaining constant.

Polymerization of the polymer in solution in the absence of monomer in accordance with the third step of procedure under the invention is preferably carried out under such conditions that the removal of solvent is prevented or with the continuous or periodic replacement of lost solvent. Best results are obtained by polymerization in the presence of a polymerization catalyst such as an organic or inorganic peroxide. Benzoyl peroxide is the preferred peroxide catalyst. Examples of other peroxide catalysts are acetyl peroxide, benzoyl acetyl peroxide, lauryl peroxide, dibutyryl peroxide, succinyl peroxide, tertiary butyl hydroperoxide (sometimes called tertiary butyl peroxide), di(tertiary alkyl) peroxides, etc. Large numbers of other catalysts are satisfactory. Mixtures of two or more catalysts can be used. The amount of catalyst will ordinarily be between about 0.1% and 5% by weight of polymer al-

though not necessarily limited to this range. In some cases it is desirable to have a polymerization inhibitor present and one or more polymerization inhibitors can be used concurrently with one or more polymerization catalysts. In still other cases it is unnecessary to use any catalyst at all.

Temperatures of from about 50° C. to about 250° C. or higher can be used. Where a catalyst is present the narrower range of from about 50° C. to about 100° C. is preferred.

The fourth step of the procedure in accordance with the invention comprises substantially completing the polymerization, preferably with the production of a hard infusible product. The product of the third step which comprises a solution of polymer in an inert solvent can be used directly in coating, impregnating, laminating, casting, and like operations with or without added solvent or non-solvent diluent or the original solvents can be wholly or partly replaced by one or more other solvents. If desired, the solution can be emulsified or otherwise dispersed in a suitable medium. The solution or solution-containing suspension can be applied by dipping, brushing, spraying, roller coating or other known or special methods to many kinds of surfaces, e. g. metal, wood, stone, paper, woven fabric, felted fabric, plastics, etc.

The coating, impregnated material or the like can then be heated with the simultaneous removal, e. g. evaporation of solvent and infusibilization of polymer. The evaporation of solvent may be assisted by the application of reduced pressure. If desired the solvent can be first removed without substantial further polymerization of the polymer, e. g. by evaporation under reduced pressure and/or by heating at below temperatures sufficient to cause further polymerization. Fusible polymer in the presence or absence of solvents or non-solvent liquids can be used for compression molding, injection molding, extrusion, etc. In some cases, particularly in the production of laminates, castings and the like, the polymerization can be completed under superatmospheric pressures. Completion of the polymerization can be hastened by higher temperatures than those employed in the first and/or third steps of procedure in accordance with the invention. Temperatures of from about 150° C. to about 250° C. are preferred although higher or lower temperatures can be used. Catalysts the same as or different from those employed in the previous steps may be present. Additional catalysts may be added. Cross-linking agents may be present.

The various steps of procedure in accordance with the invention can be carried out in a continuous or batchwise manner. In any or all of the steps the polymerizable material can, if desired, be protected from the atmosphere by blanketing with an inert gas such as carbon dioxide, nitrogen and the like or by other means. In addition to modifiers of the types already mentioned, the polymers with which the invention is concerned may be modified by plasticizers, stabilizers, lubricants, dyes, pigments, synthetic drying oils, natural resins, alkyd resins, oil modified alkyd resins, phenol aldehyde-type resins, urea aldehyde-type resins, synthetic linear polyamides, synthetic linear polyesters, synthetic linear polyester-amides, plastics and elastomers produced by the polymerization of one or more polymerizable unsaturated compounds or derived from the resulting polymers, protein plastics, cellulose derivatives, etc. Substances which do not react with or adversely affect the reactants of the invention or adversely alter the course of the polymerization may be added before or during the polymerization. These and others may be added subsequently thereto.

The following examples are given for the purpose of illustrating the invention. Parts are on a weight basis.

Example I

Diallyl phthalate was polymerized in bulk in the absence of a catalyst by being heated at about 250° C. for 2½ hours with constant stirring in the presence of carbon dioxide. The refractive index (n 20/D) increased from an initial value of 1.5208 to a final value of 1.5436. The resulting solution of monomer and partial polymer was then subjected to distillation at 180° C. under a pressure of 1 mm. of mercury. The residue was a partial polymer of diallyl phthalate obtained as a hard yellow solid.

45 parts of the partial polymer were dissolved in a mixture of 1.3 parts of methyl isobutyl ketone, 13.4 parts of toluene and 40.3 parts of xylene. 2 parts of benzoyl peroxide were added. The solution was placed in a sealed vessel and heated for 10 hours at 65° C. The viscosity at 25° C. increased from a Gardner-Holdt value of B— to V—. The viscosity of the solution was adjusted to its original value (B—) by the addition of more solvent.

A sheet of steel which had been cleaned and degreased by being boiled with trisodium phosphate was dipped into the solution and baked at 210° C. for 10 minutes. The resulting coating weighed 1.3 mg. per sq. cm. It was glossy, smooth, hard and free from pock marks and pin holes. Divinyl phthalate, dichloroallyl phthalate, diallyl diglycolate and diallyl sulfonyl diglycolate are treated similarly.

A second solution of the monomer-free partial polymer of diallyl phthalate was prepared using the same proportions of methyl isobutyl ketone, toluene, xylene and benzoyl peroxide as in the solution described above. However, this second solution was not heated to further polymerize the soluble polymer, but rather, was applied directly to a steel panel for comparison with the heat-treated solution. The steel panel had also been degreased by boiling with trisodium phosphate. The solution was applied by dipping and the coated panel was then baked at 210° C. for 60 minutes. While the baked film was hard, it was rough and pitted in contrast to the smooth, glossy film obtained from the above-described solution which had been given the preliminary heat treatment.

Example II

A solution of partially polymerized monomer-free diallyl phthalate in methyl isobutyl ketone, toluene and xylene in the same proportions as used in Example I was mixed with 0.9 part benzoyl peroxide and heated for 25 hours at 65° C. in a sealed vessel. The viscosity increased from a Gardner-Holt value of B— to T+. The viscosity of the solution was adjusted to its original value (B—) by the addition of more solvent.

A steel panel degreased by treatment with trisodium phosphate was coated with the solution by dipping and baked at 210° C. for 60 minutes. The resulting coating which weighed 1.1 mg. per sq. cm. was glossy, smooth, hard and substantially free from imperfections.

A second solution of the monomer-free partial

polymer was used to coat a degreased panel by dipping. This solution was prepared using similar proportions of the same solvents together with a like amount of benzoyl peroxide, but it was not subjected to the heat treatment for further polymerization of the partial polymer before being applied to the panel. After baking the coated panel for 60 minutes at 210° C., it was found that the baked coating was rough and pitted.

Example III

Dimethallyl phthalate is polymerized in bulk in the presence of 0.01% of tertiary butyl peroxide at 150° C. to just below the point of gel formation. The solution is poured into methanol to precipitate the polymer. The polymer is separated by filtration, washed and dried. 100 parts of the polymer are dissolved in a mixture of methyl isobutyl ketone 1.3 parts, toluene 13.4 parts and xylene 40.3 parts. The solution is heated for 10 hours at 65° C. Additional solvent is then added to adjust the solution to its original viscosity. The solution is applied as a coating to steel panels and baked at 200° C.

Example IV

A mixture of diallyl phthalate, 90 parts, and diallyl diglycolate, 10 parts, is copolymerized with heat in the absence of catalyst to just below the point of gel formation. Unreacted monomer is removed from the mixture of monomer and partial polymer. The partial polymer is dissolved in an organic solvent and further polymerized in the presence of benzoyl peroxide, following which the viscosity of the solution is adjusted to its original value by the addition of more solvent. The solution is used in the production of baked coatings. Copolymers of diallyl phthalate, dimethallyl phthalate and diallyl diglycolate are used similarly.

Example V

A monomer-free partial polymer of diallyl phthalate is produced in accordance with the first paragraph of Example I. A solution is prepared of the partial polymer admixed with soluble glycol maleate alkyd resin in an organic solvent. Benzoyl peroxide is added and the solution is heated at about 65° C. under such conditions that the loss of solvent is prevented. The viscosity of the solution is adjusted to its original value by the addition of solvent. Part of the solution is used in the production of baked coatings. Another part of the solution is used in impregnating fabric sheets, which are then superimposed forming a laminated article, and baked. Other resins similarly treated and used include mixtures of monomer-free diallyl phthalate with soluble glycerol phthalate alkyd, glycerol maleate alkyd, glycol adipate alkyd, and glycerol adipate alkyd.

Example VI

A catalyst-containing solution of diallyl phthalate partial polymer produced in accordance with the first and second paragraphs of Example I is used in impregnating unbleached muslin fabric. A plurality of plies of the impregnated fabric are superimposed. The laminate is cured under a pressure of one pound per square inch at temperatures increasing from 75° C. to 125° C. over a period of 8 hours.

We claim as our invention:

1. A process for obtaining a composition suitable for application as coating on surfaces of articles which comprises heating and further polymerizing at 50° C. to 100° C. in the presence of a peroxide polymerization catalyst a soluble polymer of a diallyl ester of a dicarboxylic acid in a solution consisting of 75 to 125 parts by weight of an inert volatile aromatic solvent per 100 parts of the polymer, said solution being substantially free of monomer of said ester; continuing said heating and further polymerizing while maintaining the proportion of solvent to polymer constant; interrupting the polymerization after appreciable further polymerization has occurred as evidenced by substantial increase in viscosity of said solution, but prior to formation of the gel polymer; and subsequently adding sufficient of said solvent to the solution of the further polymerized polymer to reduce the viscosity of the solution to approximately the viscosity which the solution had prior to the further polymerization treatment.

2. A process for obtaining a composition suitable for application as coating on surfaces of articles which comprises heating and further polymerizing at 50° C. to 100° C. in the presence of a peroxide polymerization catalyst a soluble polymer of diallyl phthalate in a solution consisting of 75 to 125 parts by weight of an inert volatile aromatic solvent per 100 parts of the polymer, said solution being substantially free of monomer of said ester; continuing said heating and further polymerizing while maintaining the proportion of solvent to polymer constant; interrupting the polymerization after appreciable further polymerization has occurred as evidenced by substantial increase in viscosity of said solution, but prior to formation of the gel polymer; and subsequently adding sufficient of said solvent to the solution of the further polymerized polymer to reduce the viscosity of the solution to approximately the viscosity which the solution had prior to the further polymerization treatment.

3. A process for obtaining a composition suitable for application as coating on surfaces of articles which comprises heating at 65° C. in the presence of 2% by weight of added benzoyl peroxide a solution having an initial Gardner-Holdt viscosity of B at 25° C. and consisting by weight of 45% of substantially monomer-free soluble polymer of diallyl phthalate, 1.3% of methyl isobutyl ketone, 13.4% of toluene and 40.3% of xylene, said heating being effected without removal of said solvents from said solution of the polymeric diallyl phthalate and said heating being continued until the viscosity of said solution has increased to a Gardner-Holdt viscosity of V at 25° C., but interrupted prior to formation of the gel polymer, and subsequently adding sufficient of said solvents to the solution of further polymerized polymer to give a solution having a Gardner-Holdt viscosity of B.

4. A process for obtaining a composition suitable for application as coating on surfaces of articles which comprises heating and further polymerizing at 50° C. to 250° C. in the presence of a peroxide polymerization catalyst a soluble polymer of an organic ester containing 2 to 4 ethylenic double bonds which are unconjugated with respect to carbon in a solution consisting of 75 to 125 parts by weight of an inert volatile organic solvent per 100 parts of the polymer, said solution being substantially free of monomer of said ester; continuing said heating and further polymerizing while maintaining the proportion of solvent to polymer constant; interrupting the

polymerization after appreciable further polymerization has occurred as evidenced by substantial increase in viscosity of said solution, but prior to formation of the gel polymer; and subsequently adding sufficient of said solvent to the solution of the further polymerized polymer to reduce the viscosity of the solution to approximately the viscosity which the solution had prior to the further polymerization treatment.

5. A process for obtaining a composition suitable for application as coating on surfaces of articles which comprises heating and further polymerizing at 50° C. to 100° C. in the presence of a peroxide polymerization catalyst a soluble polymer of a diallyl ester of a dicarboxylic acid in a solution consisting of 75 to 125 parts by weight of an inert volatile organic solvent per 100 parts of the polymer, said solution being substantially free of monomer of said ester; continuing said heating and further polymerizing while maintaining the proportion of solvent to polymer constant; interrupting the polymerization after appreciable further polymerization has occurred as evidenced by substantial increase in viscosity of said solution, but prior to formation of the gel polymer; and subsequently adding sufficient of said solvent to the solution of the further polymerized polymer to reduce the viscosity of the solution to approximately the viscosity which the solution had prior to the further polymerization treatment.

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