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ESTERS OF METHACRYLIC ACID

Harold J. Barrett and Daniel E. Strain, Wilmington, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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The present invention relates to new materials, to methods for their preparation, and more particularly to the esters of methacrylic acid with the unsaturated alcohols, and more particularly the esters of methacrylic acid with mono- or polyhydric aliphatic and/or aromatic substituted unsaturated alcohols.

An object of the present invention is to provide new compositions of matter and a process for their preparation. A further object of the invention is to provide a new polymerizable composition of matter together with a process for its polymerization. A still further object of the invention is to provide a process for the preparation of the methacrylic acid esters of the mono- and polyhydric aliphatic and/or aromatic unsaturated alcohols, which may be obtained by the ester interchange method of interacting a lower ester of methacrylic acid with the alcohol in the presence of a suitable catalyst, or by the reaction of the alcohol with a methacrylyl halide. Another object of the invention is to provide mixtures or interpolymers of the polymerized resin with other polymerizable compounds of methacrylic and acrylic acids. Other objects and advantages of the invention will hereinafter appear.

There have been prepared in accord with this invention valuable esters of methacrylic acid which have been found useful as prepared and even more valuable when polymerized. These compounds may be generally described as methacrylic acid esters of the unsaturated alcohols, such, for example, as vinyl alcohol, allyl alcohol, crotonyl alcohol, propargyl alcohol; the alkyl substituted allyl alcohols, such, for example, as methyl allyl alcohol, ethyl allyl alcohol, etc.; oleyl alcohol, alcohols made by the hydrogenation of the China-wood and castor oil acids and esters in accord with the process described in the copending Lazier application Ser. No. 584,575, filed January 2, 1932, and homologous unsaturated alcohols.

The following specific examples are furnished to illustrate methods of preparing the new compositions of matter but it will be understood that the invention is not limited to the details therein given.

Example 1.—200 parts (all parts are by weight) of oleyl alcohol, 350 parts of methyl methacrylate, 275 parts of benzene, 23 parts of hydroquinone, and 5 parts of p-toluene sulfonic acid were mixed and warmed on the water bath until solution was complete. The solution was then heated on an oil bath which was maintained at a temperature

of 130–140° C. under a 48" fractionating column fitted with a condenser arranged for controlled reflux. The distillate, which consisted of a benzene-methanol binary was collected at such a rate that the temperature at the head of the column remained at 58–59°. Heating was continued until the temperature at the head of the column could not be maintained at 58–59° C. The progress of the reaction was followed by measuring the amount of methanol in the distillate as shown by the portion that would dissolve in water. The cold reaction mixture was neutralized and then washed and dried over a suitable desiccating medium. The solvents were removed from the dried product by fractional distillation, and the ester finally separated by fractionation under reduced pressure. A 79% yield of oleyl methacrylate was obtained.

Example 2.—The process of Example 1 was repeated with 400 parts of methyl methacrylate, 264 parts of alcohols obtained by hydrogenating China-wood oils, 375 parts of benzene, 40 parts of hydroquinone, and 13 parts of p-toluene sulfonic acid 4H₂O. The temperature of the oil bath was maintained at approximately 125–130° C. and after 8 hours 91% yield of a mixture of methacrylates of the China-wood oil alcohols was obtained, which had an iodine number of 155 (theoretical for two reactive double bonds 152) and a saponification number of 159 (theoretical for isolinoleyl methacrylate is 168), and density at 20° C. of 0.915.

Example 3.—108 parts of methyl allyl alcohol, 600 parts of methyl methacrylate, 450 parts of dry benzene, and 30 parts (all parts are by weight) of phenylene diamine were mixed and heated to boiling on an oil bath under a 48" column. After the solution had started to boil the addition of approximately 12 parts of the catalyst comprising a 20% sodium methylate solution in methanol was started, and it was added in small portions at short intervals while the reaction was being carried out on an oil bath maintained at a temperature of approximately 135–142° C. The catalyst solution was added from a dropping funnel thru a side neck in the reaction flask. The course of the reaction was followed by measuring the amount of methanol (water soluble portion) in the distillate. The addition of catalyst was stopped a short time before the theoretical amount of methanol was obtained. The cold reaction mixture was dried over a suitable desiccating medium; the solvents removed by fractional distillation and the resulting mixture fractionated under reduced pres-

sure. A 60% yield of methyl allyl methacrylate was obtained, which had a boiling point of 57–59° C. at 15 mm., a density at 20° C. of 0.9214, and a saponification number of 398,—theoretical 400.

Other methods may, of course, be employed for the preparation of the enumerated methacrylates, such, for example, as are disclosed in the copending applications of Barrett and Strain Serial Nos. 735,274 and 735,275, filed on even date with this application or by any of the well known esterification or ester interchange processes.

The methacrylates as prepared in accord with the examples are usually mobile liquids, but may sometimes be solids. The esters as thus produced are monomeric and may be polymerized, according to the invention, by means of heat, light, and/or a catalyst, e. g. as described for the polymerization of organic vinyl esters in British specification 15271/1914. Preferably a catalyst such as oxygen, ozone, an organic peroxide, an ozonide, etc., is employed. Other catalysts which may be used include aluminum sulfate, boron fluoride, the mineral acids, e. g. hydrochloric and sulfuric acids, as well as the organic acids, for example, acetic and methacrylic acids, etc., as well as the anhydrides and acid halides of such organic acids, metal salts of fatty acids and resinic acids, e. g., cobalt linoleate and resinic acid, manganese oleate and rosin, etc. The polymerization may be effected in the presence or absence of a solvent for both monomer and polymer, or in the presence of a solvent for the monomer and a non-solvent for the polymer, or the monomer may be emulsified and then polymerized. Preferably polymerization is carried out at a moderate temperature, i. e. between 60–100° C., altho higher temperatures, such as, for example, 130° C., or higher, may be employed. The polymerization reaction is usually strongly exothermic and it may be necessary to control the temperature by cooling devices, tho polymerization may be carried out in apparatus which may or may not be provided with condensing devices, or in suitable pressure equipment.

As indicated, various methods may be employed for polymerizing the monomeric esters of methacrylic acid and it has been found that the properties of the resins, the physical properties to a large extent and the chemical properties to a lesser extent, are altered considerably by the type of polymerizing process utilized. The process described in the copending applications of D. E. Strain, Ser. Nos. 668,080 filed April 26, 1933 and 704,753 filed Dec. 30, 1933, may be used, if desired.

Methods illustrating the polymerization of the esters will now be described, but it will be understood that other suitable polymerizing processes may be employed.

Example 4.—Undiluted oleyl metacrylate monomer containing 1.9% benzoyl peroxide was heated to a temperature of 100° C. After 2 days the oleyl metacrylate polymer was obtained in a yield of approximately 94. The resin had the appearance of art gum rubber and was relatively insoluble in butyl acetate, gasoline, acetone, and toluene.

Example 5.—40 parts (parts are given by weight) of methyl allyl metacrylate monomer was dissolved in 300 parts of methanol in a bottle provided with a stopper, then 0.4 part of powdered benzoyl peroxide was added to this solution. After the benzoyl peroxide was all dissolved, 60 parts of water insufficient to cause

permanent turbidity was added. The bottle was securely closed and set in an oven at approximately 65° C. After the polymerization was complete in approximately 4 days, the mixture was allowed to cool. The product was filtered, washed with a little cold methanol and dried in a vacuum desiccator. The polymer was obtained in 100% yield as a very voluminous white powder which was relatively insoluble in butyl acetate, gasoline, acetone, and toluene, and was likewise infusible.

Valuable products may be obtained by utilizing the polymers of the esters described herein together with equivalents or homologues thereof admixed with other polymeric, acrylic, or metacrylic esters or other derivatives. Especially valuable products result if the monomeric esters are mixed and then polymerized; by this method interpolymers having a wide range of characteristics are made. Due to the unique characteristics of methyl methacrylate polymer, which is a hard resin having a high melting point, its admixture with the polymeric esters of methacrylic acids herein described or interpolymers thereof are particularly well adapted for many uses.

The polymerized esters of methacrylic acid, as well as mixtures or interpolymers thereof with other polymerizable compounds, are particularly well suited for thermoplastic molding. The monomer may be polymerized and/or preformed prior to placing in the mold and then may be molded in accord with the usual procedural steps employed, particularly in the molding of methyl methacrylate as described in the Rowland Hill U. S. Patent No. 1,980,483. The mold preferably is hot, prior to the introduction of the polymerization product, is then closed and the material so confined heated and pressed, the temperatures ranging from approximately 80–150° C., and pressures from 200 pounds per square inch, upward, are usually sufficient to give a suitably molded product. The presence or absence of plasticizers will, of course, alter considerably the molding conditions and it is usually advantageous to have present plasticizers to alter the physical characteristics of the resulting product to fit the particular need for which the molded article is to be used.

The masses resulting from polymerization can immediately (i. e. in the state they have been obtained) be made into useful articles. It is possible to obtain the required articles if, for instance, the polymerization be carried out while the initial material is in a suitable mold, for instance one of steel or glass, so that the articles, for example, umbrella handles, fountain pen barrels, buttons, and the like, are obtained directly from the mold. Or, if desired, the masses may be worked to the required shape by softening with suitable softeners or plasticizers in the presence of volatile solvents and, after shaping, evaporating the solvent.

The polymerization products may be worked into the required shapes in various ways; for example, they can be softened and kneaded, rolled, compressed, drawn into wires, threads or the like, or the masses can be mixed with additional substance, and rolled into plates, or films, or they may be pressed into the required shapes, such as buttons, combs, and the like.

The solid masses can be worked by cutting, sawing, filing, or the like, whether they be obtained directly by polymerization or after special treatment of the polymerized masses. These shaped

articles may be polished, and parts connected together by smearing the faces to be connected with a suitable solvent, such as acetone, epichlorhydrin, or the corresponding methacrylic acid ester.

The polymerization product dissolved in a suitable solvent which may or may not be the monomer may be transformed into a useful article, e. g. films by casting and then evaporating the solvent, or by extruding thru a suitable orifice into a precipitating bath or drying atmosphere. The polymer may be recovered from such solutions by precipitation with a suitable non-solvent for the polymer.

The properties of the resulting masses may be widely varied by modification with plasticizers, e. g. dibutyl phthalate, tricresyl phosphate, etc., drying, semi-drying and non-drying oils, synthetic and natural resins, waxes, bitumens, cellulose derivatives, e. g. cellulose nitrate and ethyl cellulose, etc., pigments, fillers, and dyes, etc. Thus it is possible to produce instead of hard glass-like masses, also soft and flexible masses. Likewise, by the addition of suitable coloring means, it is possible to produce masses, or objects, having any desired color effects; the incorporation of the additions can be effected either before, or during, the polymerizing process, or the additions can be made to the already formed polymerization products in a suitable condition.

If the polymerization of an organic methacrylic acid ester be carried out in an incomplete manner, a syrupy solution of the polymerization product containing some unchanged methacrylic acid ester is obtained. This product can be utilized either directly, or along with other solvents, or diluents, for the production of substances to be used for coating, painting, or impregnating purposes. If, for instance, a porous substance such as wood, paper, textile fabric, artificial stone, or the like be coated with the said syrupy solution or be impregnated therewith, very resistant coating and impregnations are obtained on completing the polymerization of the coating, painting, or impregnation, for instance by exposing the article to artificial or natural light or by heating it, or employing both light and heat. In this case a portion of the unchanged methacrylic acid ester in the syrupy solution may or may not be evaporated while another portion may be converted into the solid polymerization product. The articles thus treated have imparted to them a very high resistance to external influences, e. g. resistance to water, acids, alkalis and atmospheric changes.

The said syrupy mass can be mixed with comminuted matter, such, for instance, as ground cork, or ground wood, fibrous substances, mineral fillers, or the like, and the mixture be made into the proper shape and the unchanged methacrylic acid esters in the articles be converted by suitable polymerization into the solid final product.

It is also possible to start from solid, semi-solid, or plastic polymerization products of the methacrylic acid esters, these being softened by heating them by themselves, or with suitable solvents, and using them in their softened state. On cooling or on the evaporation of the diluent, that may still be present, the product is converted into the solid lacquer-form.

It is obvious that mixtures of various polymerized methacrylic acid esters can be used for lacquering, painting, or impregnating in accordance with this invention. It is likewise obvious

that the wholly, or partly, polymerized esters can be mixed with suitable additional substances to modify the properties of the lacquering, painting, or impregnating materials in any desired manner. As additions of this kind oils should be mentioned (such, for example, as castor oil), dyes, powdered substances (such as zinc oxide), camphor, camphor substitutes, and the like.

In accordance with this invention it is possible to obtain valuable products if the said polymers be dissolved, or softened, in suitable solvents and then be converted again to the solid state. The products thus obtained may be used for purposes for which cellulose esters have hitherto been used, namely, as substitutes for horn, amber, artificial resins, lacquers, for impregnation purposes, and also for the production of films, interlayer for safety glass, pressure adhesives, artificial threads, and the like.

The products thus formed have the advantage over products made from nitrocellulose in being less inflammable. By the addition of suitable agents the strength and hardness of the products may be modified within wide limits so that it is possible to manufacture both hard, horn-like substances and soft and more pliable products. The products may also be modified by varying the conditions of the polymerization.

The monomer may be polymerized in the presence of a solvent and the solution used as such or the polymer recovered from the solution by evaporation or precipitation methods. In many cases, however, it is more profitable to use an amount of solvent insufficient to produce a freely flowing solution, so that soft plastic masses are obtained which can be pressed, kneaded, rolled or drawn into shape, or formed into blocks, plates, or films.

Plasticizers or other modifying agents may be added to the monomer prior to polymerization or directly to the polymerized product, it being generally desirable to employ a plasticizer which is soluble in the polymer and the monomer, altho it is not essential that the dual solubility characteristics be present. Thus, plasticizers or softening agents, such as, for example, camphor; phthalates, such as ethyl, propyl, isopropyl, butyl, isobutyl, cyclohexyl, methyl cyclohexyl, or benzyl phthalate or phthalates of the mixed type, such as cyclohexyl butyl, benzyl butyl or butyl lauryl phthalate; esters of other dibasic acids, such as the ethyl, propyl, isopropyl, butyl, isobutyl, cyclohexyl, methyl cyclohexyl or benzyl esters of succinic, fumaric, tartaric, adipic and sebacic acids; esters of monobasic acids, such as the butyl, isobutyl, cyclohexyl, methyl cyclohexyl, benzyl or lauryl esters of lauric, laevulinic, benzoic, benzoyl propionic and benzoyl benzoic acids; esters of polyhydric alcohols, e. g. glycol and glycerol, such as glycol benzoate, glycol laevulinate, triacetin, tripropionin and tributyrin; substituted toluene sulphonamides, such as ethyl paratoluene sulphonamide; substituted amides, such as tetraethyl, phthalamide, tetrabutyl succinamide, tetrabutyl adipamide, tetraethyl phthalamide; hydrocarbons, such as dixyl ethane; halogenated hydrocarbons, such as chlorinated diphenyls and dichloridibenzyl; ether compounds such as dicresoxy ethyl ether; and drying, non-drying, or semi-drying oils, such as castor oil, cotton seed oil, linseed oil, and the like. These additions also facilitate later mechanical treatment, as cutting, sawing, and polishing.

The polymers of the unsaturated alcohol esters of the methacrylic acid and interpolymers thereof

with other methacrylic, acrylic and vinyl esters are generally insoluble and infusible. The fact is of great importance in the production of novel products which are especially resistant to the action of solvents and high temperatures. This unique property may be utilized to advantage by polymerizing the monomer (with or without diluent, plasticizer, and catalyst) in situ in a suitable container or mold conforming to the shape desired.

Shaped articles, moreover, can be prepared by polymerizing the monomer in suitable molds with heat and pressure. As an alternate process the monomer may be polymerized in such a manner that a solid polymer mass is obtained from which articles can be machined or cut.

Articles with both rigid and flexible backings can be given a finishing coat of high gloss and resistivity to solvents by coating or impregnating the backing with monomer and conducting the polymerization of the monomer in situ. The coating or impregnation may be done from the monomer alone, from a solution of monomer, or an emulsion containing the monomer. The polymerization may be conducted by exposing the coated or impregnated backing to heat and/or light. The coating of metal, wood, stone, glass, shaped plastics, or rigid articles made from or coated with cellulose derivative compositions, resins, and the like illustrate the broad application of the above idea to rigid surfaces. The coating or impregnating of cloth, paper, wire mesh, rubber, leather, regenerated cellulose films, and the like illustrates application to flexible backings.

Compositions suitable for the production of shaped articles and/or the coating or impregnating of both rigid and flexible surfaces may comprise the monomer alone, mixtures of monomer, with or without the addition of polymerization catalysts, plasticizers, resins, cellulose derivatives, pigments, dyes, fillers, etc.

The polymerized esters, mixtures of the polymerized esters with dissimilar polymerizable esters or other polymerizable compounds of methacrylic or acrylic acids, or vinyl compounds; or interpolymers of the esters with such other compounds, may be used advantageously as safety glass interlayers. These polymerized esters, mixtures thereof, or interpolymers thereof may be plasticized or otherwise modified as desired. The compositions may be compounded with glass in an unpolymerized, partially polymerized or completely polymerized condition. When compounding the safety glass with the unpolymerized or partially polymerized compositions, the polymerization may be effected by subjecting the sandwich of glass and compound to suitable application of light and/or heat.

From a consideration of the above specification it will be realized that various changes may be made in the process or product without departing from the invention or sacrificing any of its advantages.

We claim:

1. Oleyl methacrylate.

2. Polymeric oleyl methacrylate.

3. The polymeric methacrylic acid ester of an unsaturated alcohol selected from the group consisting of vinyl alcohol, allyl alcohol, crotonyl alcohol, propargyl alcohol, methyl allyl alcohol, ethyl allyl alcohol, oleyl alcohol and alcohols made by the hydrogenation of China-wood and castor oil acids and esters, prepared by heating the monomeric ester to a temperature of from 60 to 130° C., in the presence of benzoyl peroxide.

4. The polymeric methyl allyl methacrylate prepared by heating the monomeric ester at a temperature of from 60 to 130° C., in the presence of benzoyl peroxide.

5. The molding composition comprising a polymeric methacrylic acid ester of an unsaturated alcohol selected from the group consisting of vinyl alcohol, allyl alcohol, crotonyl alcohol, propargyl alcohol, methyl allyl alcohol, ethyl allyl alcohol, oleyl alcohol and alcohols made by the hydrogenation of China-wood and castor oil acids and esters, prepared by heating the monomeric ester to a temperature of from 60 to 100° C., in the presence of benzoyl peroxide.

6. The molding composition of claim 5 in admixture with a plasticizer therefor.

7. The interpolymer of a methacrylic acid ester of an unsaturated alcohol selected from the group consisting of vinyl alcohol, allyl alcohol, crotonyl alcohol, propargyl alcohol, methyl allyl alcohol, ethyl allyl alcohol, oleyl alcohol and alcohols made by the hydrogenation of China-wood and castor oil acids and esters, with a polymerizable compound of the group consisting of acrylic acid and methacrylic acid derivatives, which interpolymer is prepared by polymerizing a mixture of the monomeric compounds at a temperature of from 60 to 130° C., in the presence of benzoyl peroxide.

8. A process for the preparation of a polymeric ester of an unsaturated alcohol selected from the group consisting of vinyl alcohol, allyl alcohol, crotonyl alcohol, propargyl alcohol, methyl allyl alcohol, ethyl allyl alcohol, oleyl alcohol and alcohols made by the hydrogenation of China-wood and castor oil acids and esters, which comprises heating a solution, of the methacrylate monomer selected from the group, containing benzoyl peroxide and water to a temperature of approximately 65° C. and holding it at that temperature until polymerization is substantially complete.

HAROLD J. BARRETT.

DANIEL E. STRAIN.