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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 aliphatic monohydric saturated straight and branch chain primary alcohols. An object of the present invention is to provide a new composition of matter and a process for its 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 aliphatic monohydric saturated straight and branch chain primary alcohols containing more than five carbon atoms in the molecule, 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. Another object is to provide methacrylic acid esters, such, for example, as the methacrylate of stearyl, lauryl, cetyl, myristyl alcohols and the like. 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 aliphatic monohydric saturated straight and branch chain primary alcohols containing more than five carbon atoms in the molecule such, for example, as methacrylic acid esters of the primary straight and branch chain hexyl, heptyl, octyl, nonyl, decyl, dodecyl, and higher equivalent and homologous substituted or unsubstituted alcohols, such as halogen or amino substituted alcohols of the class, for example, betadiethyl amino ethanol; stearyl alcohol, lauryl alcohol, cetyl alcohol, myristyl alcohol, the mixture of primary alcohols obtained by the catalytic hydrogenation of carbon oxides under elevated temperatures and pressures having more than five carbon atoms, obtained in accord with the process described in the Roger Williams U. S. Patent No. 1,844,847, or any process producing similar products, the mixture of primary alcohols, containing more than five carbon atoms, obtained from the catalytic hydrogenation of coconut and like oils, in accord with the Lazier process described in his copending application Ser. No. 520,473 filed March 5, 1931, which discloses a process for the preparation of alcohols by the catalytic hydrogenation of glycerides under elevated temperature and pressure, or by any suitable process for the hydrogenation of those oils, and other equivalent 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.—186 parts of lauryl alcohol were mixed with 400 parts of methyl methacrylate, 2.9 parts of concentrated sulfuric acid and 24 parts of hydroquinone (all parts are given by weight) and the resulting mixture heated on the water bath until the solution was complete. The solution was then heated on an oil bath, held at a temperature of approximately 150° C. under a 48" fractionating column fitted with a condenser arranged for controlling reflux. Distillate was collected at such a rate that the temperature at the head of the column remained at the boiling point of the methanol-methyl methacrylate binary (64°). 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 41.3% yield of lauryl methacrylate was obtained. It had a boiling point of 142° C., at 4 mm., and a saponification number of 215,—theoretical 221.

Example 2.—The process of Example 1 was repeated with 800 parts of methyl methacrylate, 372 parts of a mixture of alcohols obtained by the hydrogenation of coconut oil, 6 parts of concentrated sulfuric acid, and 45 parts of hydroquinone. The temperature of the oil bath was maintained at approximately 150–160° C., and after 4 hours a 51% yield of the methacrylic acid ester was obtained. This ester had a density at 20° C. of 0.874 and a saponification number of 214.

Example 3.—153 parts of a mixture of oxygenated organic compounds boiling between 133–147° C., obtained by the catalytic hydrogenation of carbon oxides, 600 parts of methyl methacrylate, 350 parts of benzene, 35 parts of hydroquinone, and 12 parts of p-toluene sulfonic acid, 4H₂O, are mixed and warmed on a water bath until solution was complete. The solution was then heated on an oil bath 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 suit-

able desiccating medium. The solvents were removed from the dried product by fractional distillation, and the ester finally separated by fractionation under reduced pressure. A 25% yield of a mixture of methacrylic esters of the oxygenated compounds was obtained. The esters had a boiling range of 67–70° C. at 9 mm., a density of 0.880 at 20° C., and a saponification number of 295.8.

Example 4.—The process of Example 3 was repeated with 400 parts of methyl methacrylate, 270 parts of stearyl alcohol, 300 parts of benzene, 3.5 parts of sulfuric acid (concentrated) and 30 parts of hydroquinone. The temperature of the oil bath was maintained at approximately 140–150° C., and after 7 hours a 75% yield of stearyl methacrylate was obtained. The ester had a melting point of 28–29° C., and a saponification number of 157,—theoretical 166.

Example 5.—100 parts of betadiethyl amino ethanol, 340 parts of methyl methacrylate, 450 parts of dry benzene, and 20 parts of p-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 the catalyst, a methanol solution containing 20% sodium methylate, 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 130–145° C. The total catalyst added was approximately 20 parts. 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 generally stopped a short time before the theoretical amount of methanol was obtained. The product was neutralized, dried, vacuum distilled and freed from betadiethyl amino ethanol by repeated extraction with water. A 52% yield of betadiethyl amino ethyl methacrylate was obtained.

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 Ser. Nos. 735,275, 735,276 and 735,278, filed on even date with this application and disclosing processes for preparing methacrylates by treating alcohols with monomeric acid halides and monomeric methacrylic acid esters of the lower alcohols, or by any of the well known suitable 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 15,271/1914. 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 and more particularly 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 resinate, 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. or higher, may be employed. The polymerization reaction is usually strongly exothermic and it may be necessary to control the temperature by cooling devices, the 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 6.—43.5 parts (parts are given by weight) of lauryl methacrylate monomer was dissolved in 189.2 parts of methanol in a bottle provided with a stopper, then 0.5 part of powdered benzoyl peroxide added to this solution. After the benzoyl peroxide was all dissolved, 13 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 48 hours, the mixture was allowed to cool. The liquid was decanted. The resin was removed from the bottle, was cut into small pieces and was dried in a vacuum desiccator. The polymer was obtained in a 90% yield as a colorless, sticky, very viscous liquid resin which was relatively insoluble in all common solvents.

Example 7.—The polymerization process of Example 6 was repeated using 100 parts of the monomer obtained from the raw material and by the process of Example 2, 310 parts of methanol, 1 part of benzoyl peroxide, and 4 parts of water. After 5 days at 65° C., an 80% yield of a fused, transparent, amber colored, rubber like, very sticky, polymer was obtained which was relatively insoluble in all common organic solvents.

Example 8.—The polymerization process of Example 6 was repeated using 20 parts of monomer obtained from the raw material and by the process of Example 3, 150 parts of methanol, 0.2 part of benzoyl peroxide, and 30 parts of water. After 1 day at 65° C., a 90% yield of the polymer was obtained as fused, glassy, particles which were soluble in toluene and relatively insoluble in butyl acetate, gasoline and acetone. A 5% solution in toluene gave a viscosity of 0.024 poise at 25° C. The polymer is compatible with nitrocellulose.

The resin was placed in a disk shaped mold in which it was subjected to a temperature of 100° C., and a pressure of approximately 5,000 pounds per square inch for approximately 15 minutes. A water-clear molded disk was obtained which softened at a temperature of 32° C.

The compatibility with nitrocellulose was determined by dissolving an equal volume of a 5% toluene solution of the polymerized ester in a solution consisting of 20 parts of nitrocellulose and 380 parts of butyl acetate. The resulting

solution was spread on a glass plate and allowed to dry at room temperature.

Example 9.—Undiluted stearyl methacrylate monomer containing 1% benzoyl peroxide was heated to a temperature of 65° C. After 48 hours the polymer was obtained as a hard, brittle wax which upon heating becomes transparent and slightly rubber-like at about 38° C. The polymer was relatively insoluble in all common organic solvents.

Example 10.—Undiluted diethyl aminoethyl methacrylate monomer containing no polymerizing catalyst polymerizes at low temperatures very readily, in fact polymerization has occurred at temperatures as low as 0° C. Polymerization for 18 hours at 100° C., produced a 100% yield of a bubble-free, amber colored, transparent, firm but rubbery, slightly tacky polymer which gelled in toluene but was relatively insoluble in butyl acetate, gasoline and acetone.

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 methacrylic esters or other derivatives. Especially valuable products result if the monomeric esters are mixed prior to their polymerization; 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 esters of methacrylic acid are particularly well suited for thermoplastic molding. The ester 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 pending application, Serial No. 641,113. 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 through 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 by 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 there may be mentioned oils (such, for instance, 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 slower burning and odorless. 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; the ether alcohol esters of the polycarboxylic acids, e. g., methoxy ethyl and ethoxy ethyl phthalate; substituted toluene sulphonamides, such as ethyl paratoluene sulphonamide; substituted amides,

such as tetraethyl phthalamide, tetrabutyl succinamide, tetrabutyl adipamide, tetraethyl phthalamide; hydrocarbons, such as dixylyl ethane; halogenated hydrocarbons, such as chlorinated diphenyls and dichlorodibenzyl; 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 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. A mixture of methacrylic acid esters of the mixture of primary, straight and branch chain alcohols obtained by the catalytic hydrogenation of carbon oxides under elevated temperatures and pressures.

2. A new composition of matter comprising a mixture of methacrylic acid esters of the mixture of primary straight and branch chain alcohols obtained by the catalytic hydrogenation of carbon oxides under elevated temperatures and pressures and having a boiling range of 67-70° C., at 9 mm.

3. A polymeric mixture of methacrylic acid esters of the mixture of primary, straight and branch chain alcohols obtained by the catalytic hydrogenation of carbon oxides under elevated temperatures and pressures.

4. An interpolymers of a methacrylic acid ester of an aliphatic monohydric saturated primary alcohol containing more than five carbon atoms in the molecule and another polymerizable compound selected from the group consisting of a derivative of acrylic acid and a derivative of methacrylic acid.

5. A process for the preparation of a methacrylic acid ester of an aliphatic monohydric saturated primary alcohol containing more than 5 carbon atoms in the molecule, which comprises reacting methyl methacrylate with an aliphatic monohydric saturated primary alcohol containing more than 5 carbon atoms in the molecule.

6. An interpolymers of a methacrylic acid ester of an aliphatic monohydric saturated primary alcohol containing more than five carbon atoms in the molecule and another polymerizable ester of methacrylic acid.

HAROLD J. BARRETT.
DANIEL E. STRAIN.