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COMPOSITIONS AND PROCESS

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This invention relates to polymers of esters of alpha methacrylic acid which are soluble in petroleum oils or in petroleum distillates and particularly in petroleum hydrocarbons having a substantially aliphatic character and to the process for preparing these esters.

In my copending application Serial No. 729,699, filed June 8, 1934, I have shown that certain polymerized esters of acrylic and alpha methacrylic acid are soluble in high boiling petroleum hydrocarbons such as lubricating oils, etc.

The present invention deals particularly with joint polymers of two or more esters of methacrylic acid at least one of which esters, when polymerized alone, will form a polymer insoluble in petroleum hydrocarbons. It is known that the methyl and ethyl esters of alpha methacrylic acid when polymerized individually or jointly with each other, form transparent bodies of high molecular weight. These polymers are readily soluble in aromatic hydrocarbons such as benzene or toluene, but are practically insoluble in aliphatic hydrocarbons such as gasoline, petroleum naphtha, vaseline, paraffin oils or paraffin wax. This is likewise true of the polymerized propyl, allyl, butyl and chloroethyl esters of alpha methacrylic acid. Beginning with the amyl ester, increasing the length of the alcohol radical increases the solubility of the polymer in petroleum hydrocarbons, so that although the amyl ester is sparingly soluble in heavier hydrocarbons, such as lubricating oils, it is practically insoluble in the lighter ones, such as petroleum naphtha, or varnish makers' and painters' naphtha.

For many purposes, however, it is desirable to make solutions of these polymers in such petroleum products as varnish makers' and painters' naphtha or any other similar petroleum distillates, or at least to form solutions of them in aromatic hydrocarbons from which they are not precipitated by the addition of large proportions of the petroleum hydrocarbon.

I have found that the polymerized monohydric aliphatic alcohol esters of alpha methacrylic acid having more than five carbon atoms in the alcohol radical are readily soluble in petroleum hydrocarbons of substantially aliphatic character, provided the polymerization has not been carried too far. Practically all of these esters may be polymerized to such an extent that they become insoluble even in the aromatic hydrocarbons but if the esters of the higher alcohols are polymerized to such an extent that they are still soluble in aromatic hydrocarbons, they will also be soluble in petroleum hydrocarbons. In my copend-

ing application Serial No. 757,456 filed December 14, 1934, now Patent No. 2,100,993, I describe a convenient process for preparing these higher aliphatic esters of α -methacrylic acid.

I have also found that the lower monohydric aliphatic alcohol esters of alpha methacrylic acid, in which the alcohol radical contains from 1 to 5 carbon atoms when polymerized jointly with a higher monohydric aliphatic alcohol ester of alpha methacrylic acid containing 6 or more carbon atoms in the alcohol radical, preferably 10 to 18 carbon atoms inclusive, give polymers which are readily soluble in aliphatic hydrocarbons or which are not readily precipitated from their solutions in aromatic hydrocarbons by the addition of a large proportion of petroleum hydrocarbons. For instance if a mixture of equal parts of ethyl alpha methacrylate and cetyl alpha methacrylate are polymerized jointly at 80° C. for 16 hours in the presence of 0.2% of benzoyl peroxide, the resulting product is a tough, transparent, colorless material which is the joint polymer of the two components and which is readily soluble in varnish makers' and painters' naphtha. If ethyl alpha methacrylate were polymerized alone under the same conditions, it would be completely insoluble in the same solvent. Furthermore, if one part of polymerized ethyl alpha methacrylate were mixed with one part of polymerized cetyl alpha methacrylate a physical mixture would result which when added to petroleum naphtha would be separated, leaving the polymerized ethyl alpha methacrylate as an insoluble residue.

This process of copolymerizing a lower with a higher monohydric aliphatic alcohol ester of alpha methacrylic acid containing more than 5 carbon atoms in the alcohol radical will thus produce new polymers having useful properties in coating or laminated compositions, since cheap petroleum solvents can be used for preparing their solutions instead of the more expensive aromatic solvents. Such solutions in petroleum naphtha are particularly useful in coating compositions because they may be painted directly over oleoresinous coatings without lifting the latter.

The lower esters of methacrylic acid yield hard products on polymerization, whereas the higher esters such for instance as lauryl, cetyl, oleyl and octodecyl esters yield soft, rubbery, elastic masses. It is thus possible to vary the hardness and elasticity of the product by jointly polymerizing a suitable mixture of the different esters. When one of the esters of the joint polymer has

a very long alcohol chain, a larger proportion of the ester of the lower alcohol can be used. Thus for instance, in a mixture of cetyl alpha methacrylate and ethyl alpha methacrylate a larger proportion of the latter can be used than in a mixture of hexyl alpha methacrylate and ethyl alpha methacrylate and still yield a joint polymer which is soluble in petroleum hydrocarbons.

10 In practicing this invention, a suitable mixture of the esters is preferably polymerized at 70 to 100° C. in the presence of a catalyst such as benzoyl peroxide. Although heating is the preferred method of polymerizing the esters described herein, other methods may be employed
15 such as exposure to light, pressure, heat and pressure, etc. Catalysts other than benzoyl peroxide may also be used, including both organic and inorganic peroxides such as acetyl peroxide, hydrogen peroxide, etc. The polymerization may
20 also be carried out if desired, in the presence of a solvent or the initial materials may be emulsified in water and polymerized in the emulsified state.

25 The following examples will illustrate the invention, but this is not to be limited to the exact materials or conditions given excepting as defined by the appended claims:

Example 1.—100 grams of ethyl alpha methacrylate and 200 grams of lauryl alpha methacrylate were mixed and heated for 18 hours at 75° C. in the presence of 0.6 grams of benzoyl peroxide until a colorless transparent product was obtained. The product was a very tough elastic
35 solid completely soluble in varnish makers' and painters' naphtha.

Example 2.—A mixture of 20 grams of ethyl alpha methacrylate and 10 grams of n-octadecyl alpha methacrylate and 0.06 grams of benzoyl peroxide was heated at 75° C. for 18 hours. A colorless product was obtained. A solution of a part of this product in 5 parts of toluene was prepared and to this solution was added 100 parts of varnish makers' and painters' naphtha. No
45 precipitation of the polymer took place at this dilution.

Example 3.—A mixture of 100 grams of methyl alpha methacrylate and 120 grams of cetyl alpha methacrylate containing 0.4 grams of benzoyl peroxide was heated at 80° C. until a solid, colorless polymer was formed. The product was very tough but completely soluble in lubricating oil or in paraffin wax.

Example 4.—A mixture of 100 grams of ethyl alpha methacrylate and 150 grams of oleyl alpha methacrylate containing 0.4 grams of benzoyl peroxide was heated for 18 hours at 75° C. The product obtained was a colorless, tough, rubbery mass which dissolved readily in petroleum naphtha.

Example 5.—A mixture of 25 grams of ethyl alpha methacrylate, 25 grams of n-butyl alpha methacrylate and 50 grams of cetyl alpha methacrylate containing 0.5 grams of benzoyl peroxide
65 was heated for 16 hours at 80° C. The product obtained was a colorless, rubbery, mass readily soluble in petroleum naphtha.

The ethyl or methyl alpha methacrylate shown in the foregoing examples may be replaced by propyl, butyl, allyl or amyl, alpha methacrylate or mixtures thereof. Generally speaking the larger the number of carbon atoms, in the alcohol radical of the lower ester, the lower the proportion of the higher ester required. Likewise the cetyl, lauryl, oleyl or octadecyl alpha

methacrylate can be replaced by the n-hexyl, n-octyl or n-decyl esters or mixtures thereof. In this instance also, the shorter the alcohol chain in the higher ester, the lower the proportion of the lower ester which can be jointly polymerized
5 in order to yield a product soluble in petroleum hydrocarbons.

The products prepared as described above find many uses in the arts. They may be used as insulating media for heat or electrical insulation, simply by surrounding the object to be insulated with the polymerized material. They find use as general adhesives. In employing these products for this purpose, they may either be used in solution or in the form of a preformed sheet. In the case of the latter, the ordinary method of cementing objects together is to place the preformed sheet between the objects and subject the composite product to heat and/or pressure. It has been found that the monomeric materials may be placed between the two objects and the polymerization completed in situ with consequent cementing together of the two objects. Of special interest in the use of the products as adhesives, are the cementing together of metal to metal, glass to glass, glass to metal, the cementing of textiles to textiles or to any other materials, etc.

The products also serve as coating and impregnating materials for textiles, leather and other fibrous materials, including wood, paper, etc. In impregnating fabrics the polymerized products may be employed or the fabric may be impregnated with the monomeric materials with polymerization taking place in situ by the application of heat or other polymerizing influences. The products also find application as the intermediate layer in the manufacture of laminated glass, either alone or with other adhesive materials. Molded objects can also be prepared from the products of this invention.

The products may be made in the form of sheets, slabs, blocks or rods and in many other shapes. In emulsified form they find many uses, such as coating compositions for leather, etc. They are also useful as plasticizers for cellulose derivatives and when incorporated with alkyd resins improve the adhesion, toughness, color and flexibility of the resins.

They may be added to animal, vegetable and mineral oils as thickeners. In the textile field the products aid in rendering textiles crease-proof. For the preparation of materials suitable for use as coating compositions, etc., they may be incorporated with rubber or rubber latex. On incorporation with phenol formaldehyde resins, greater shock-proofness is obtained than can be obtained by the use of phenol formaldehyde resins themselves. They may be used to coat and impregnate paper and can be used on stencil sheets and duplicating papers in conjunction with waxes and dyes. In printing inks they act as a stiffener.

Furthermore, the products herein described can be used as glass substitutes for various purposes, including the manufacture of optical lenses for goggles, etc.

I claim:

1. A co-polymer of at least two different monohydric aliphatic alcohol esters of alpha-methacrylic acid, one of which contains less than six carbon atoms in the alcohol radical and another more than five carbon atoms in the alcohol radical.

2. A co-polymer of two different monohydric aliphatic alcohol esters of alpha-methacrylic acid,

one of which contains less than six carbon atoms in the alcohol radical and the other from 12 to 18 carbon atoms inclusive in the alcohol radical.

3. A co-polymer of two different monohydric aliphatic alcohol esters of alpha-methacrylic acid one of which contains less than six carbon atoms in the alcohol radical, and the other from 12 to 18 carbon atoms inclusive in the alcohol radical, said co-polymer being a colorless, rubbery mass, soluble in petroleum hydrocarbons.

4. A co-polymer of ethyl-alpha-methacrylate and lauryl alpha methacrylate, said co-polymer being soluble in petroleum hydrocarbons.

5. A co-polymer of ethyl alpha methacrylate and cetyl-alpha methacrylate, said co-polymer being soluble in petroleum hydrocarbons.

6. A co-polymer of ethyl alpha methacrylate and n-octa-decylalpha methacrylate, said co-polymer being soluble in petroleum hydrocarbons.

7. A co-polymer of ethyl-alpha methacrylate and an aliphatic monohydric alcohol ester of alpha methacrylic acid containing from 6 to 18 carbon atoms, inclusive, in the alcohol radical.

8. A process for preparing co-polymers of esters of alpha methacrylic acid which are soluble in substantially aliphatic petroleum hydrocarbons, which comprises polymerizing a mixture of at least two different aliphatic monohydric alcohol esters of alpha methacrylic acid, one of which contains less than six carbon atoms in the alcohol radical and another more than five carbon atoms in the alcohol radical.

9. A process for preparing co-polymers of esters of alpha methacrylic acid which are soluble in substantially aliphatic petroleum hydrocarbons, which comprises heating a mixture of at least two different aliphatic monohydric alcohol esters of alpha methacrylic acid, one of which contains less than six carbon atoms in the alcohol radical and another more than five carbon atoms in the alcohol radical.

10. A process for preparing co-polymers of

esters of alpha methacrylic acid which are soluble in substantially aliphatic petroleum hydrocarbons, which comprises heating a mixture of at least two different aliphatic monohydric alcohol esters of alpha methacrylic acid, one of which contains less than six carbon atoms in the alcohol radical and another more than five carbon atoms in the alcohol radical, at 70 to 100° C. in the presence of benzoyl peroxide.

11. A process for preparing co-polymers of esters of alpha methacrylic acid which are soluble in substantially aliphatic petroleum hydrocarbons, which comprises heating a mixture of ethyl alpha methacrylate and lauryl alpha methacrylate at 70-100° C. in the presence of benzoyl peroxide.

12. A process for preparing co-polymers of esters of alpha methacrylic acid which are soluble in substantially aliphatic petroleum hydrocarbons, which comprises heating a mixture of ethyl alpha methacrylate and cetyl alpha methacrylate at 70-100° C. in the presence of benzoyl peroxide.

13. A process for preparing co-polymers of esters of alpha methacrylic acid which are soluble in substantially aliphatic petroleum hydrocarbons, which comprises heating a mixture of ethyl alpha methacrylate and n-octadecyl alpha methacrylate at 70-100° C. in the presence of benzoyl peroxide.

14. A process for preparing co-polymers of esters of alpha methacrylic acid which are soluble in substantially aliphatic petroleum hydrocarbons, which comprises heating a mixture of ethyl alpha methacrylate and an aliphatic monohydric alcohol ester of alpha methacrylic acid having six to eighteen carbon atoms inclusive in the alcohol radical at 70-100° C. in the presence of benzoyl peroxide.

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

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