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ANTISTATIC AGENTS FOR HYDROPHOBIC FIBER

Robert William Rimmer, Newark, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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8 Claims. (Cl. 117—139.5)

This invention relates to novel compositions of matter which are useful as antistatic agents for hydrophobic textile fiber. More particularly, this invention deals with novel olefine-type interpolymers of diverse esters of acrylic or methacrylic acid, as more fully defined below.

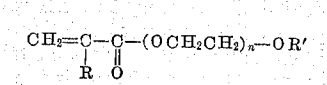
It is an object of this invention to produce novel organic compounds which are useful as treating agents for textile fiber. A special object of this invention is to provide antistatic agents of improved qualities for hydrophobic textile fibers, such as nylon, polyethylene terephthalate fibers, polyacrylonitrile fibers, hydrophobic cellulose derivatives and their various modifications.

Fibers of the aforementioned types are well known for their poor electrical conductivity. As a result, they tend to accumulate electrostatic charges in working, as for instance in the textile mill, or in service, as for instance in a rug. Such charges may be annoying, for instance, by causing a nylon dress to cling to the body of the wearer, interfering with the intended graceful hang of the garment; but they are worse than annoying in the textile mill, where such static charges, formed through repeated friction of the fiber, filament or yarn, may prevent proper spinning, drawing, twisting, weaving or knitting.

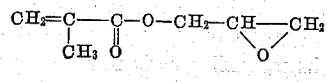
It has already been proposed in the art to overcome the above noxious tendency by treating the fiber with various antistatic agents, whose action apparently depends on the ability of the agent to conduct electricity by a process of ionization. The difficulties encountered in the selection of a proper antistatic agent have been aptly enumerated in U. S. Patent No. 2,676,122, wherein the solution offered to the problem consisted of selecting certain alkanolamine salts of long-chain alkyl phosphates as therein specified.

However, as the commercial use of antistatic agents is being developed, certain new requirements are continuously added to the problem. One such requirement is durability to washing and cleaning. In other words, it is required that the antistatic effect shall be fast to washing (with water), laundering (in water, with soap) and dry cleaning (with organic solvents).

I have now found that antistatic agents of excellent initial strength and of satisfactory durability to washing and dry cleaning are obtained by polymerizing the novel monoalkoxy polyethylene glycol acrylates of Formula I hereinbelow in the presence of a minor quantity of glycidyl methacrylate. The copolymer thus obtained is of the olefinic type, and the components thereof consist of (I) a monoalkoxy polyethylene glycol acrylate of the formula



wherein R designates H or CH_3, R′ is a lower alkyl radical (i. e. an alkyl radical of 1 to 6 C-atoms), while the subscript n has a value not less than 4 and not greater than 20, and (II) glycidyl methacrylate, which may be represented by the formula



Component II is selected in minor proportions, say 2% to 25% by weight, with respect to component I.

The esters constituting component I are themselves novel compounds and are described more fully and claimed in the copending application of Harold S. Holt, Serial No. 530,896, now Patent 2,815,369, issued December 3, 1957. In a general way, they may be prepared by transesterification of a lower alkyl acrylate or methacrylate with a lower-alkyl monoether of a polyethylene glycol of the formula $HO—(CH_2CH_2O)_n—R'$, wherein R′ and n have the same significance as above. Or they may be prepared by reacting a monoalkyl ether of a polyethylene glycol as above defined with the acid chloride of acrylic or methacrylic acid.

The initial monoalkyl ethers themselves are generally obtained by a process of polymerization; that is, by reacting with ethylene oxide gas upon a lower monoalkyl ether of ethylene or diethylene glycol. The resulting reaction product therefore consists of a mixture of monoalkyl polyethylene glycols of the above formula with various integral values of n. The value of n in the initial material and in the resulting acrylate esters is thus an average number, and may have integral as well as fractional values.

Some of the initial monoalkyl polyethylene glycols occur in commerce. Thus, methyl ethers of total molecular weights of 550 and 750, and designated in commerce as "methoxy polyethylene glycol 550" and "methoxy polyethylene glycol 750" are available on the market. The average value of n in these compounds is therefore approximately 12 and 16, respectively. Others can be readily synthesized by the method above indicated.

The interpolymerization of components I and II according to this invention may be achieved by known general methods, for instance by heating the two components together in a common solvent, for instance water, alcohol, dioxane, mixtures of these, tetrahydrofurane, benzene, etc., in the presence of a free-radical polymerization catalyst. As suitable instances of the latter may be mentioned dibenzoyl peroxide, ammonium or potassium persulfate, azo-bis-isobutyronitrile, and cumene hydroperoxide, although other similar compounds may also be used. Conventional amounts of such polymerization catalysts (or "initiators," as they are sometimes called) are 0.1% to 0.5% based on the joint weight of components I and II.

The reaction temperature is generally determined by the activity of the catalyst selected; that is, a temperature is selected at which the catalyst will generate free radicals. Conversely the catalyst may be selected on the basis of the temperature at which the reaction is to be operated, so that free radicals will be obtained at that temperature. The reaction is operable at room temperature and can be run as high as 85° to 100° C., especially in organic media. In water, however, it is preferable not to go above 50° to 60° C., because the polymer is less soluble in water at higher than at lower temperatures.

The polymerization system should preferably be about neutral, but it can be slightly acidic or alkaline; i. e., it may have a pH of 4.5 to 8.

Control is exercised to produce a polymer which is soluble enough to be padded onto the fiber from an aqueous, alcoholic or aqueous-alcoholic solution or suspension, but which is nevertheless sufficiently polymerized to be converted to an insoluble finish upon curing the fiber. Curing implies heating the treated fiber at temperatures generally in the range of 105° to 150° C. The insolubilization caused by curing is believed to be due to cross-linking of the polymer.

It is important to avoid gelation in the process of

producing the interpolymer. Control to this effect may be achieved by one or both of the following remedies:

(1) Adding initially a modifier such as 2-mercaptoethanol, which moderates the chain growth; and

(2) Holding down the reaction temperature to a value not exceeding about 100° C.

The quantity of modifier, when employed, is generally of the order of 1 to 5 mols percent, based on the polyethylene glycol ester employed.

The physical qualities of the resulting copolymer depend not only on the ratio of components I and II, but also on the value of *n* in the former. The polymers resulting when *n* is relatively low, say 4 to 6, are soluble in benzene and other non-polar solvents, and also, to some extent, in water. But as the value of *n* increases, the polymer becomes increasingly soluble in polar media.

Essentially all copolymers of the above nature (regardless of the value of *n*) give an excellent initial, and to some extent durable, antistatic rating on the cured fiber; but exceptional durability of this effect to repeated launderings generally begin at $n=6$ and increases with the value of *n*.

The application of the above copolymers to textile fiber is preferably done by padding from an aqueous bath, followed by squeezing out the excess moisture, drying, and curing the fiber at a temperature between 105° and 150° C. for a period, varying inversely with the temperature, from 20 to 3 minutes.

The padding bath may be an aqueous, aqueous-alcoholic or aqueous-dioxane solution of the polymer, if the latter is soluble enough, or an aqueous suspension if the polymer is not sufficiently soluble. The padding bath will generally contain from 1 to 5% of the polymer by weight, and the impregnated goods will generally be squeezed until they retain about 0.5 to 2.5% of the active ingredient by weight based on the weight of the fiber. Higher concentrations or higher retentions of the active ingredient are tolerable, however, except for considerations of economy.

The cured finish is fast to washing with water, with or without soap, and to dry cleaning (with solvents) in the absence of detergents.

When the treated fiber is polyacrylonitrile, improved abrasion resistance is incidentally imparted to the fiber, and the effect is reasonably fast to washing.

It is remarkable that all the aforenoted effects are obtained with little if any stiffening of the fiber.

For the purpose of measuring the electrostatic qualities of fabrics treated with my novel agents, the following procedure for testing and the table of ratings hereinbelow have been adopted as standards.

Testing procedure.—A strip of fabric 3 cm. wide is cut from the sample to be tested and its electrical resistance at a controlled relative humidity of 25% is measured on a special apparatus which comprises two electrodes separated by a space of 1.25 cm. and having a potential difference of 90 volts. The fabric is held in place between the electrodes so as to provide a conducting area 1.25 cm. long and 3 cm. wide. The direct measurement gives the resistance of the mentioned area in ohms. Multiplication of this measurement by 2.4 gives the so-called "resistivity per sq. cm." of the tested fabric. This resistivity is then translated into an antistatic rating according to the following table:

Resistivity per sq. cm.	Antistatic Rating
(0 to 1,000)×10⁸ ohms	Excellent.
(1,000 to 10,000) ×10⁸ ohms	Very good.
(10,000 to 50,000)×10⁸ ohms	Good.
(50,000 to 125,000)×10⁸ ohms	Fair.
(125,000 to 500,000)×10⁸ ohms	Poor.
Above 500,000×10⁸ ohms	Nil.

Without limiting my invention the following examples are given to illustrate my preferred mode of operation. Parts mentioned are by weight.

PART A.—PREPARATION OF THE MONOALKOXY POLYETHYLENE GLYCOL ACRYLATES

Example 1

A solution was prepared containing 48.2 g. of methacrlyl chloride, 150 g. of methoxy polyethylene glycol of M. W. 320, 37.9 g. of pyridine and 400 ml. of ether. The charge was warmed to reflux for one hour. Approximately one-half of the ether was then distilled off and the mass was filtered to remove the pyridine hydrochloride. Distillation was then continued and finished under vacuum until all the ether was removed. The weight of the residual ester was 148 g It was a colorless, oily liquid, soluble in water, alcohol and dioxane.

Example 2

85 g. of the product marketed as methoxy polyethylene glycol "550," 86 g. of methyl acrylate and 50 mg. of p-tertiary butylcatechol were mixed together. The resulting solution was heated to boiling and 25 g. of methyl acrylate was distilled off, until the head temperature reached 79° C. 0.5 g. of tetraisopropyl titanate was then added to the system, and over the next 5 hours, 60 g. of a mixture of methyl acrylate and methyl alcohol were distilled off. An additional quantity of methyl acrylate was then removed until the pot temperature reached 130° C., at which point the ceric nitrate test for alcohol on the distillate indicated no more than a trace of methyl alcohol in the system. The charge was then cooled to 90° C., and residual methyl acrylate was removed under vacuum. 83.5 gms. of methoxy polyethylene glycol acrylate were obtained. The product had the same physical appearance and chemical properties as in Example 1.

Example 3

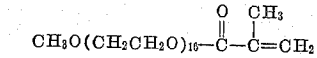
825 g. of methoxy polyethylene glycol "550," 825 g. of methyl methacrylate, 9.27 g. of nitrobenzene and 0.927 g. of 2,6-di(t-butyl)-p-cresol were heated with agitation under nitrogen to the boil, and methyl methacrylate and water were removd by distillation, until the head temperature reached 99.5° C. After cooling, 7.4 g. of tetraisopropyl titanate were added, and upon resuming heating the methyl alcoholmethyl methacrylate azeotrope which formed was removed. Another portion of tetraisopropyl titanate (1.8 g.) was added, and distillation was continued until the head temperature reached 99° C. At this point the distillation gave only a faint ceric nitrate test for alcohol and reaction was considered complete.

The charge was then cooled to 95° C., under nitrogen, and 37 ml. of distilled water were added with stirring. The mass was steam distilled to remove methyl methacrylate. After cooling the residual mass to room temperature, its weight was brought up to 1840 g. by adding distilled water. The content of methoxy polyethylene glycol methacrylate in the mass was found by bromine titration to be 48.5% by weight.

Example 4

A mixture of 750 g. of commercial, methoxy polyethylene glycol "750" and 775 g. of thiophene-free benzene was distilled until the weight of the residual mass reached 975 g. To the thus dried solution were added 500 g. of distilled methyl methacrylate containing 2.0 g. of nitrobenzene and 0.2 g. of phenothiazine. The mixture was stirred and heated to reflux. Benzene was removed until the column and still head were free of moisture. At this point 3.0 g. of tetraisopropyl titanate were added and the column was put on total reflux. Over the next 2½ hours 80 g. of benzene-methyl-alcohol azeotrope were collected. 1.0 g. of tetraisopropyl titanate was then added and distillation was continued for an additional hour, until a ceric nitrate test showed no

alcohol in the distillate. The charge, weighing 1186 g., was then cooled to 40° C. under nitrogen. The excess benzene and methyl methacrylate were removed by distillation under reduced pressure, until the pot temperature reached 87° C. at a pressure of 0.2 mm. The residue, constituting methoxy polyethylene glycol methacrylate of the formula



exhibited the same physical and chemical properties as the product of Example 1.

Example 5

Following the general procedure of Example 1, equivalent amounts of n-hexyloxy-decaethylene-glycol and methacrylyl chloride were reacted in ether solution, in the presence of enough pyridine to react with the HCl formed. The precipitated pyridine hydrochloride was filtered off, the ether evaporated and the monomer dispersed in water as a 30% emulsion. This monomer is soluble in water up to about 5%.

The initial n-hexyloxy-decaethylene-glycol was prepared by condensing hexyl alcohol and ethylene oxide in known manner, using a sodium catalyst.

PART B.—PREPARATION AND TESTING OF THE INTERPOLYMERS

Example 6

15 g. of the ester obtained in Example 1 above and 0.8 g. of glycidyl methacrylate were dissolved in 23.7 g. of water and adjusted by means of alkali to pH 7. The solution was heated to 65° C. under nitrogen and then 20 mg. of ammonium persulfate, $(NH_4)_2S_2O_8$, were added. After one hour, the solution became very viscous and finally gelled.

The gel was dissolved in a mixture of 12 g. of tetrahydrofuran and 60 g. of dioxane, and was diluted with water to produce a 4% concentration by weight of the copolymer.

"Dacron" polyester fabric was padded with this solution, then dried and cured at 110° C. for 5 minutes, and finally washed in 0.5% aqueous soap solution at 160° F. for 30 minutes with agitation.

The fabric thus treated was tested for antistatic action directly after curing, after one soaping and after three soapings.

It was found to possess a rating of excellent directly after curing; very good, after the first soaping; and still good, after three soapings.

The rating of untreated "Dacron" polyester fabric on the same scale is "nil."

Example 7

A solution of 83.5 g. of the methoxy polyethylene glycol acrylate obtained in Example 2 and of 12.5 g. of glycidyl methacrylate in 96 g. of water was adjusted to pH 7 and then heated to 60° C. under nitrogen. 150 mg. of ammonium persulfate were added in small increments over a period of 2 hours. The viscosity started to increase rapidly; so over the next hour period water was fed into the mass gradually while continuing the heating, until the concentration of the polymer in the reaction was diluted to 10%.

The aqueous reaction mass was then cooled and diluted further to produce a 4% aqueous treatment bath. When "Dacron" polyester fabric was padded from this bath, squeezed to a 50% wet pick-up (2% solids on weight of fabric), dried and cured at 140° C. for 5 minutes, it acquired an antistatic quality of rating excellent. The antistatic effect was still excellent after one soaping (in 0.5% aqueous soap solution at 160° F. for 30 minutes), and very good after 5 soapings.

The treated fabric was also subjected to repeated dry cleanings (in perchlorethylene) and found to be of excellent antistatic rating after 1 cleaning and still very good after five such cleanings.

Example 8

4210 g. of a 57% aqueous solution of the methoxy polyethylene glycol methacrylate obtained in Example 3 were diluted with 7790 g. of water and adjusted with sodium hydroxide solution to pH 7.1. The solution was placed in an autoclave under an atmosphere of nitrogen; 15 g. of 2-mercapto ethanol were added; the mass was heated under agitation to 50° C., and 240 g. of glycidyl methacrylate were added. 40 cc. of a 5% aqueous potassium persulfate solution (adjusted to pH 8) were then added, and additional portions of the same catalyst solution were added in small portions over a period of 5½ hours until a total of 275 cc. has been entered. A commercial anti-foaming agent was added in small portions from time to time as tendency to foam was observed. The mass was then kept at 50° C. for an additional five hours, at which point consumption of the monomer, as determined by bromine titration, was 90% complete. The mass was then again adjusted to pH 7 by the aid of sodium hydroxide and finally diluted with water to a 20% concentration of the polymer.

The resulting solution had a viscosity of 2000 cps. and a density of 1.03; both at 25° C. When "Dacron" polyester fiber was padded with an aqueous bath diluted to 4% polymer concentration and alkalized to pH 10, then dried and cured at 120° C. for 3.5 minutes, it acquired an antistatic effect of rating excellent, which remained very good after 10 washings in 0.5% soap solution.

Polyacrylonitrile fiber and "nylon" fiber, when treated in the same manner, acquired a similar high degree of antistatic protection.

Example 9

A solution of 100 g. of the product of Example 4 and 25 g. of glycidyl methacrylate in 375 g. of diethylcarbitol was heated to 75° C. under nitrogen. 30 mg. of α,α'-azo-bis-isobutyronitrile were added. After 20 min. another 10 mg. of the catalyst were added. After 2 hours 150 mg. of hydroquinone was stirred into the thick mass to stop the polymerization, and the copolymer was then bottled as a 23% active-ingredient solution.

When "Dacron" polyester filament fabric was padded from a 5% solution of the above polymer dried and cured at 140° C. for 5 min., it acquired antistatic protection of rating very good, which did not drop materially after 5 launderings with soap.

Example 10

98 g. of methoxy-deca(ethyleneoxy)-methacrylate (prepared from methoxy decaethylene glycol and methacrylyl chloride according to the general procedure of Example 1 above) were dissolved in 400 g. of water. 2 g. of glycidyl methacrylate and 0.5 g. of ammonium persulfate were added, and the mass was heated at 65° C. for 16.5 hours. As polymerization proceeded, the viscosity of the reaction mass increased until it finally set into a gelled mass of 20%-solids concentration. By the aid of vigorous stirring, the reaction mass was dispersed in water to a concentration of 4%. The particle weight of the dispersed polymer was determined to be between 600,000 and 700,000.

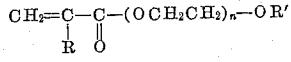
Evaluation of this composition on "Dacron" polyester fiber showed it to be an effective antistatic agent with durability through 20 laundering cycles. The hand of the treated fabrics was soft and pliable and was unaffected by continued laundering.

Polymers of essentially the same qualities are obtained if the 98 g. of the methacrylate in the above example are replaced by 112 parts of the n-hexyloxy-decaethyleneoxy methacrylate obtained in Example 5 above.

I claim as my invention:

1. The interpolymers obtained by polymerizing, at a

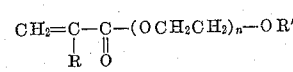
temperature not exceeding 100° C. and in the presence of a free-radical polymerization catalyst, a mixture of glycidyl methacrylate and of an ester of the formula



wherein R′ designates an alkyl radical of 1 to 6 C-atoms, R stands for a member of the group consisting of hydrogen and methyl, while the subscript *n* has a value not less than 4 and not greater than 20, the polyalkyleneoxy ester constituting the major proportion of the mixture by weight.

2. An interpolymer as in claim 1, the glycidyl methacrylate being present in proportion of 2 to 25% by weight based on the weight of the other ester.

3. A process of producing an interpolymer useful for treating textile fiber, which comprises polymerizing a mixture of glycidyl methacrylate and of an ester of the formula



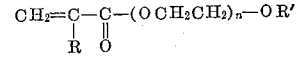
wherein R′ designates an alkyl radical of 1 to 6 C-atoms, R stands for a member of the group consisting of hydrogen and methyl, while the subscript *n* has a value not less than 4 and not greater than 20, the polyalkyleneoxy ester constituting the major proportion of the mixture by weight, at a temperature not exceeding 100° C. in the presence of 2-mercapto ethanol.

4. A process of improving the electrostatic qualities of hydrophobic textile fiber, which comprises impregnating the same with an interpolymer as defined in claim 1.

5. A process of improving the electrostatic qualities of hydrophobic textile fiber, which comprises padding said fiber with an aqueous bath containing an interpolymer as defined in claim 1, removing excess moisture from the fiber and then subjecting the latter to heating at a temperature between 105° and 150° C. for a period of time varying inversely with the temperature from 20 to 3 minutes.

6. Hydrophobic textile fiber having incorporated therein from 0.5 to 2.5% by weight of an interpolymer as defined in claim 1, said fiber being characterized by increased electrical conductivity compared to the same fiber when it does not contain said interpolymer.

7. The interpolymers obtained by polymerizing, at a temperature not exceeding 100° C. and in the presence of a free-radical polymerization catalyst, a mixture of glycidyl methacrylate and of an ester of the formula



wherein R′ designates an alkyl radical of 1 to 6 C-atoms, R stands for a member of the group consisting of hydrogen and methyl, while the subscript *n* has a value not less than 4 and not greater than 20, the glycidyl methacrylate being present in proportion of 2 to 25% by weight based on the weight of the other ester, and the free-radical polymerization catalyst being selected from the group consisting of dibenzoyl peroxide, ammonium persulfate, potassium persulfate, azo-bis-isobutyronitrile, and cumene hydroperoxide.

8. A process of improving the electrostatic qualities of hydrophobic textile fiber, which comprises padding said fiber with an aqueous bath containing an interpolymer as defined in claim 7, removing excess moisture from the fiber and then subjecting the latter to heating at a temperature between 105° and 150° C. for a period of time varying inversely with the temperature from 20 to 3 minutes.

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