United States Patent Office 2,839,430 Patented June 17, 1958

2,839,430

ANTISTATIC AGENTS FOR HYDROPHOBIC FIBER

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No Drawing. Application August 26, 1955 Serial No. 530,887

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 derivatives of acrylic or methacrylic acid, as more fully defined below.

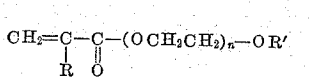
It is an object of this invention to produce novel organic compounds which are useful as treating agents for textile fiber. A special object of this invention is to provide antistatic agents of improved qualities for hydrophobic textile fibers, such as nylon, polyethylene terephthalate fibers, polyacrylonitrile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

Fibers of the aforementioned type 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.

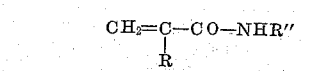
However, as the commercial use of antistatic agents is being developed, certain new requirements are continuously added to the problem. One such requirement is durability to washing and cleaning. In other words, it is required that the antistatic effect shall be fast to washing (with water), laundering (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 an acrylamide as defined below. 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) an acrylamide of the general formula



wherein R is H or CH_3, and R″ is H, CH_2OH, $CH_2—OCH_3$ or $CH_2—OC_2H_5$.

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, Patent No. 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. Curing implies heating the treated fiber at temperatures generally in the range of 105° to 150° C.

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 mole 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 polar solvents and also, to some extent, in water. But as the value of n increases, the polymer becomes increasingly soluble in water.

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 begins 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 containing formaldehyde, 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 addition of formaldehyde may be dispensed with in the case of those acrylamides which contain a methylol group or an alkoxy-methyl group on the N-atom.

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 of the polymer is not sufficiently soluble. The padding bath will generally contain from 1 to 5% of the polymer by weight, and in the case of the primary acrylamides, also from 1 to 5% of formaldehyde. The latter can be added in the form of its aqueous solution or in its other forms, such as paraformaldehyde. 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.

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 methacrylyl 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

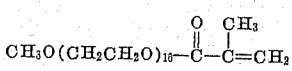
825 g. of methoxy polyethylene glycol "550," 825 g. of methyl methacrylate, 9.27 g. of nitrobenzene and 0.927 g. of 2,6-di(t-butyl)-p-cresol were heated with agitation under nitrogen to the boil, and methyl methacrylate and water were removed by distillation, until the head temperature reached 99.5° C. After cooling, 7.4 g. of tetraisopropyl titanate were added, and upon resuming heating the methyl alcohol-methyl 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 ben-

zene 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

A solution of 50 g. of the polyethylene glycol acrylate monomer of Example 2 and 2.5 g. of acrylamide in 200 g. of water was adjusted to pH 7 by the aid of sodium hydroxide solution, and heated to about 60 to 65° C. under nitrogen. After 15 minutes, 50 mg. of ammonium persulfate was added. After 4 hours another 10 mg. of catalyst in 50 g. of water was added. After a total of 8 hours of heating the polymerization was stopped by adding 100 mg. of hydroquinone and cooling. A small amount of gel had formed in the product but most of the very thick product dissolved easily in water. The product was left as an 8% active-ingredient solution.

A 5% solution of the copolymer in water was made up to contain 3% of paraformaldehyde. The pH was brought to 10 by the aid of NaOH, and the solution was allowed to stand at room temperature for 1 hour. The pH was then lowered to 3 by the addition of sulfuric acid.

"Dacron" polyester fabric was padded with this solution, then dried and cured at 140° 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 five soapings.

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

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

Example 7

A solution of 83 g. of the methoxy polyethylene glycol acrylate obtained in Example 2 and of 5.88 g. of N-methylol acrylamide in 312 g. of water was heated to 50° C. under nitrogen. Then 0.43 g. of 2-mercaptoethanol and 0.136 g. of potassium persulfate were added. The viscosity of the charge increased rapidly. Therefore the charge was diluted to 10% active-ingredient and allowed to polymerize for 4 to 4.5 hours. The product was a viscous cloudy mass with a viscosity of 17,000 cps. at 25° C. It was found to be a good antistatic agent for synthetic hydrophobic fibers and its durability properties were satisfactory.

Example 8

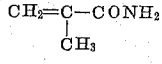
N-ethoxymethyl methacrylamide is prepared by adding concentrated sulfuric acid to an ethanol solution of methylol methacrylamide from methacrylamide and formaldehyde until pH of about 3 and then warming the mixture at 40° C. for 30 minutes. The excess acid is carefully neutralized with alkali and the excess ethanol removed by distillation.

10 parts of the product thus obtained and 50 parts of hexyloxy-hexadecaethyleneoxy methacrylate are dissolved in 250 parts of water, brought to pH 7 and polymerized over a 4 hour heating period at 50° C. The polymerization is carried out under a nitrogen atmosphere and in the presence of 0.12 part of potassium persulfate catalyst (which is added in portions as the polymerization proceeds) and in the presence of 1.0 part of 2-mercaptoethanol modifier. After the 4 hour heating period, the polymerization is stopped by adding 0.1 part of hydroquinone and cooling.

An aqueous solution of the copolymer thus obtained is made up to contain 5% by weight of copolymer and the pH adjusted to between 4 and 5. Polyacrylonitrile fabric is padded with this solution, squeezed and cured as described in Example 1. Essentially the same antistatic effects and excellent durability are obtained.

When the other monoalkoxy polyethylene glycol acrylate obtained in Examples 1 to 5 above are substituted in Examples 6, 7 and 8 above, copolymers of similar properties and durable antistatic qualities are obtained.

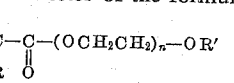
As concerns the acrylamides employed for copolymerization, they are mostly old compounds or may be prepared by known methods. Thus the primary acrylamide, $CH_2=CH-CONH_2$, is described in Beilstein, Handbuch der Organischen Chemie, 4th edition, vol. II, page 400; the synthesis of methacrylamide,



is discussed in Org. Synthesis 29, 61 (1949); N-methylol acrylamide and N-methylol methacrylamide are reported in J. A. C. S. 75, 5027, 1953. The lower alkyl ethers of N-methylol acrylamide, for instance the ethyl ether, $CH_2=CH-CONH-CH_2-OC_2H_5$ may be prepared in known manner from ethanol and N-methylol acrylamide in the presence of acid. This procedure follows that disclosed in J. Org. Chem., vol. 16, pages 1111–1115, 1951, where the corresponding ethers from the methylol amide of a fatty acid are prepared.

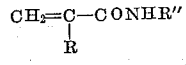
I claim as my invention:

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 an acrylamide and of an ester of the formula



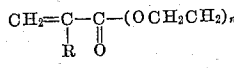
wherein R′ designates an alkyl radical of 1 to 6 C-atoms, R stands for a member of the group consisting of hydrogen and methyl, while the subscript *n* has a value not less than 4 and not greater than 20, the acrylamide being present in proportion of 2 to 25% by weight based on the weight of said ester.

2. An interpolymer as in claim 1, the acrylamide being a compound of the formula



wherein R stands for a member of the group consisting of hydrogen and methyl, and R'' represents a member of the group consisting of H, CH_2OH, $CH_2—OCH_3$ and $CH_2—OC_2H_5$.

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



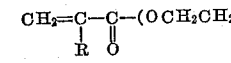
wherein R' designates an alkyl radical of 1 to 6 C-atoms, R stands for a member of the group consisting of hydrogen and methyl, while the subscript n has a value not less than 4 and not greater than 20, at a temperature not exceeding 100° C. in the presence of 2-mercaptoethanol, the acrylamide being present in proportion of 2 to 25% by weight based on the weight of said ester.

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 an acrylamide 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 acrylamide being present in proportion of 2 to 25% by weight based on the weight of the said 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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