This invention relates to polymeric anti-static agents and to textile materials treated therewith. More particularly it relates to certain polymeric alkyl sulfate quaternary ammonium salts of the acryloyloxyethylamine type.

One disadvantage of the new textile fibers and fabrics prepared from the recently introduced synthetic hydrophobic materials, and of all textile fibers treated with conventional resin finishes, is that they tend to develop a static electrical charge. This charge is objectionable during the manufacture of the textile and in the finished garment. During manufacture, the static charge on the fiber or fabric prepared therefor interferes with their convenient handling during treatment with various pieces of equipment, such as in spinning, reeling, weaving, and the like. Finished articles which are designed to drape like cotton or wool articles fail to do this properly, in that the fabrics often cling to the wearer. Furthermore, such textiles tend to collect dust and lint, and the electric discharge itself is both hazardous and unpleasant.

Many treating agents have been proposed to impart anti-static effects to textiles of this type. However, none of these proposed agents is entirely satisfactory, but all are deficient in effectiveness, either initial or sustained, and are also deficient with respect to resistance to washing and dry cleaning.

It is therefore an object of this invention to provide an effective anti-static agent which is highly resistant to washing and dry cleaning. Another object is the provision of a new class of polymeric compound which imparts a durable, anti-static effect to synthetic textile fibers and fabrics. A still further object is the treatment of textiles at any stage during the manufacture of textile fabrics with such polymeric compounds to produce the substantially permanent anti-static effect. Another object is a simple method for applying such polymeric compounds to the textile material. Other objects will appear as the description of the invention proceeds.

These and other objects are accomplished by a new composition of matter comprising (1) a polymeric salt of the type:

\[
\left[ \begin{array}{c}
\text{R} \\
\text{O} \\
\text{R}_1
\end{array} \right]
\begin{array}{l}
\text{CH}_2\text{C-}
\text{O-R_1-R_2-N-R_3-N-}
\end{array}
\begin{array}{l}
\text{R_4}
\end{array}
\begin{array}{l}
X
\end{array}
\]

where \( R \) is \( H, \text{CH}_3 \) or \( \text{CH}_2\text{H}_5 \); \( R_1 \) is a divalent hydrocarbon radical of 1 to 4 carbon atoms; \( R_2, R_3, \) and \( R_4 \) are aliphatic hydrocarbon groups of 1 to 4 carbon atoms; \( X \) is a hydrocarbon sulfonic acid salt of 8 to 20 carbon atoms; and \( n \) is greater than 10; and (2) copolymers of these with less than 75% of another ethylenically unsaturated monomer.

In the preferred compositions \( R \) is methyl, \( R_1 \) is ethylene \((-\text{CH}_2\text{CH}_2\text{H}_2-\)), at least two of \( R_2, R_3 \) and \( R_4 \) are ethyl. The alkyl subsitituent on \( X \) is preferably hexadecyl, and the composition is a homopolymer.

Among the operable comonomers are vinyl ethers of quaternary ethanol amines, vinyl acetate, doddeyl methacrylate, acrylonitrile, methacrylamide and its ethylene oxide condensates. These compositions may be conveniently prepared by a dimethil or diethyl sulfate quaternization of the appropriate acryloyloxyalkyldialkylamine in water followed by polymerization, and then reaction with a salt of an alkyl sulfate having from 8 to 20 carbon atoms in the alkyl group. This latter reaction may be carried out either in a reaction vessel or on the textile itself.

It is somewhat preferable to quaternize the tertiary amine prior to polymerization rather than afterward, since it is easier to obtain complete quaternization and also to remove any excess of the quaternizing agent.

The intermediate polymeric quaternary ammonium salt is preferably water-soluble, since it is conveniently applied to the textile surface from aqueous solution. Its anion is chosen with this property in view. Suitable quaternizing agents for reaction with the tertiary amine either before or after polymerization are alkyl halides such as methyl iodide, ethyl bromide and butyl chloride; alkyl sulfates such as dimethyl sulfate; alkyl sulfonates such as ethyl p-toluene sulfonate; alkyl phosphates such as triethyl phosphate; and alkyl phosphites such as triethyl phosphite. Specifically preferred as the intermediate is the methylsulfate salt of the quaternary ammonium compound which is obtained by reaction of the tertiary amine with dimethyl sulfate.

The polymerization or copolymerization of the monomeric vinylidene compound is carried out by any of the conventional methods, either with or without a solvent or in an emulsion. In most cases polymerization in aqueous solution is advantageous, though other hydroxylated solvents and particularly the monohydric alcohols containing from 1 to 4 carbon atoms, such as methanol and tert-butanol, are usable.

The amount of comonomer may vary from 0 to 75 wt. per cent, and in some cases to 95%, of the material to be polymerized. The choice depends on one or more factors such as economics and the desired physical properties of the polymer. If a comonomer is used, its amount generally is in the range of 5% to 75%. The time and temperature required for a substantial degree of polymerization to take place depend on the monomeric compounds and the catalyst employed, from 1 to 24 hours and from 20° to 100° C. being customary conditions. The free radical type catalysts are employed. Suitable compounds are the peroxoxygen compounds, e. g., ammonium persulfate, potassium persulfate, and benzoyl peroxide; azo compounds of the type described in U. S. 2,471,995, e. g., alpha, alpha'-azo-diisobutonitrile; combinations of thiourea with hydrogen peroxide, a bromate with a bi-sulfite, hydrogen peroxide with a titanous salt, etc. The amount of the catalyst used is generally small; e. g., 0.01–3% by weight of the polymerizable monomers. If desired, the rate of polymerization can be decreased by use of a small amount of a polymerization inhibitor such as p-tert-butyl catechol. Introduction of a trace of a dithiocarbamate salt such as sodium dimethyl dithiocarbamate will stop the polymerization at any desired stage.

The compositions of this invention are white to cream-colored brittle, waxy solids, relatively insoluble in water but somewhat more soluble in common polar organic solvents such as ethanol, acetone, ethyl acetate, dioxane, etc.

These compositions may readily be converted into the corresponding long-chain carboxylic esters, either in the reaction vessel or on the textile itself. In either event, the long-chain carboxylic acid furnishes the anion of the polymeric quaternary ammonium salt, and may be one or a mixture of saturated or unsaturated carboxylic acids containing an acyclic carbon chain of at least 8 carbon.
atoms. The preferred acids are the fatty acids containing from 12 to 22 carbon atoms such as lauric, stearic, oleic, palmitic, myristic, arachidic and behenic acids. Polymeric carboxylic acids such as the polyacrylic and polymethacrylic acids are also suitable.

The formation of the long-chain carboxylate salts results from an anion exchange reaction in which the existing anion associated with the quaternary ammonium group is displaced by the carboxylate in an aqueous solution. In order to displace a high proportion of the anions, it is desirable to use an excess of the long-chain carboxylic acid or salt, preferably at least 25% to 50% above the theoretical necessary amount. In this way a majority of pre-existing anion radicals are displaced and, ordinarily, the displacement is relatively complete, i.e. 90% or more.

The compositions of this invention are applied to textile materials by (1) padding from their solution in one of the solvents described above; (2) padding from a dilute aqueous solution (about 1% to 5%) of one of the above-described short-chain alkyl sulfate intermediates, followed by scouring with a long-chain alkyl sulfate; (3) extension of a short-chain intermediate with the aid of a long-chain alkyl sulfate, as described in copending application Serial No. 339,482, filed February 27, 1953. The temperature of the treating bath is not particularly critical, but is best at temperatures above 140°F. for a period of about 30 minutes. The textile materials to which the present invention is applicable may be in the form of fibers, filaments, yarns, or fabrics. The compounds produce anti-static effects on any organic textile fiber which has a tendency to accumulate a static charge. Many of the natural fibers and some of the synthetic fibers do not exhibit undesirable static effects and, therefore, the invention is of primary importance to synthetic organic textile materials which have high electrical resistivity and, as a result, accumulate static charges. Among the fabrics which are benefited by treatment according to the present invention are nylon, acrylic, nylon, polyethylene terephthalate fibers, and similar fibers and textiles. The salts of the present invention may also be applied to wool with advantageous results.

The invention is illustrated by the following examples, although these are given merely by way of illustration and not limitation, since any polymeric salt or cocommoner falling within the above generic definition may be used in the examples in equivalent amount.

Example I

To a stirred mixture of 55.5 parts of beta-methylacryloyloxyethyldimethyamine and 55 parts of water is added 38 parts of dimethyl sulfate over a period of 45 minutes, at 30° to 35° C. The solution is stirred for 30 additional minutes at 30° to 35° C, and is then diluted with a solution of 10 parts of sodium acetate trihydrate in 125 parts of water. The reaction mixture is heated to 50° to 55° C, and a solution of 0.4 part ammonium persulfate in 27 parts of water is added. The mixture is stirred for 20 minutes at 50° to 55° C, under a nitrogen atmosphere, during which time polymerization proceeds. At the end of this time, the greatly thickened solution is bottled. The viscosity continues to increase for several hours. After 24 hours from the beginning of the polymerization, a portion of the 50% solution is diluted to give a 1% aqueous solution and the dilute solution is padded onto fabrics of nylon, cellulose acetate, polyacrylonitrile and polyethylene terephthalate. The fabrics are heated for 3 minutes at 140° C to 160° C. The pick-up of the quaternary salt ranges from 0.25 to 0.5% by weight, based on the weight of the fabric.

These fabrics are secured with a commercial dodecyl sodium sulfate detergent in about 0.25% aqueous solution to convert the finish to the corresponding dodecyl sulfate salt. These fabrics have considerably improved anti-static properties over untreated controls.

Example II

The polymeric methiodide quaternary of Example III of Hayek Serial No. 260,119 is diluted to give a 1% solution. This is applied to fabrics composed of nylon, polyacrylonitrile and polyethylene terephthalate to give loadings of about 0.25% of the methiodide salt. These treated fabrics are then washed with a 0.5% solution of the sodium salt of a technical dodecyl sulfate (average carbon chain length C12). The coating on the textiles is thus converted into the corresponding long-chain alkyl sulfate. The anti-static ratings are fair.

Example III

The composition of Example I is also prepared in benzene, Stoddard solvent and without any solvent. In these cases, the reaction with dimethyl sulfate is followed by the addition of water and sodium bicarbonate, with which the product is agitation for 17 to 18 hours (Stoddard solvent and benzene runs) and 7 hours (without solvent) at 50° C, to destroy the excess dimethyl sulfate. During these heating periods polymerization takes place. In the benzene and Stoddard solvent run the solvent is decanted.

The products are viscous, pourable pastes to rubber-like masses difficultly soluble in water. They are evaluated by diluting with 1% active ingredient with water and applying, scouring with a 20-carbon alkyl sulfate and testing as described in Example I. The anti-static rating of each of the four fabrics is improved, and the effect is durable to washing in each case.

Example IV

A mixture of 15 parts of beta-methylacryloyloxyethyldimethyamine and 15 parts of beta-vinloxydimethyamine is made in 25 parts of benzene, containing 0.05 part of the catalyst alpha, alpha'-azido-disobutynitrilite. This mixture is stirred under nitrogen at 65° to 83° C., for 2.4 hours, during which time 0.2 part additional catalyst is added.

Then 25.2 parts of dimethyl sulfate is added over 0.5 hour at 25° to 54° C. with stirring. The quaternized polymer separates. Water (200 parts) is added and the benzene is removed by azetotropic distillation.

A 2.0% active ingredient in water is padded onto fabrics of nylon, polyacrylonitrile, polyethylene terephthalate and cellulose acetate at 0.5% loadings. The treated fabrics are secured with a 0.25% solution of the sodium salt of a technical hexadecenyl alkyl sulfate, and found to have markedly improved anti-static properties when tested as described above. The anti-static effect is very durable to soap scouring.

Example V

Example I is repeated using a 75:25 copolymer of beta-methylacryloyloxytrimethyl ammonium methylsulfate with vinyl acetate as the polymeric. Markedly improved anti-static properties are obtained. The effect is durable to washing.

Example VI

A copolymer of beta-methylacryloyloxyethyltrimethyl ammonium methysulfate (20 parts) with 6.7 parts of the methacrylate of technical lauryl alcohol is made by mixing them in the absence of air in 25 parts of benzene containing 0.1 part of alpha, alpha'-azido-disobutynitrilite and heating 4 hours at 80° to 70° C. When 12.6 parts of dimethyl sulfate is added with stirring over 6 minutes. An additional 80 parts of benzene is also added during this period to keep the reaction mass fluid enough to stir. The benzene is removed by azetropic distillation with water.

As a 1% active ingredient solution in water this product is padded onto fabrics of cellulose acetate, nylon, polyacrylonitrile and polyethylene terephthalate. The dodecyl and methiodside salts of these fabrics have considerably improved anti-static properties over untreated controls.
sodium hexadecenyl sulfate, a durable anti-static effect of satisfactory quality is produced.

Example VII

A 75:25 copolymer of beta-methacryloyloxyethylmethacrylamine and vinyl acetate is prepared by the procedure of Example IV, except that the benzene is omitted until the quaternization step. Application of the product and conversion to the dodecyl sulfate salt gives satisfactory results as in Example VI.

Example VIII

A 50:50 copolymer is made of the methiodide of betamethacryloyloxyethylmethacrylamine (20 parts) with 20 parts of 4-vinyl-pyridine, using the procedure of Example VII. About 75 parts of ethanol is added to maintain a stirrable reaction mass.

Then 21.6 parts of dimethyl sulfate is added over 12 minutes at 26° to 34° C., together with 100 parts of water, to quaternize the vinyl-pyridine portion.

The polymer is then converted to the dodecyl sulfate salt by addition of a molar equivalent of sodium dodecyl sulfate with agitation.

Example IX

A solution of 12.5 parts of the polymeric methyl-sulfate salt of Example I in 129 parts of water is added dropwise at room temperature to a stirred solution of 11.6 parts of octanol sodium sulfate in 150 parts of water. The white waxy solid which separates is removed, washed several times with water and dried under vacuum. The resulting poly-beta-methacryloyloxyethylmethacrylammonium octyl sulfate is a white amorphous solid containing 88.8% S. (theory 78.2). When a 2.0% alcoholic solution of the product is padded onto nylon and polycrylonitrile fabrics, good anti-static properties, which are durable to washing, are obtained.

Example X

Poly-beta-methacryloyloxyethylmethacrylammonium hexadecenyl sulfate is prepared by the method of Example IX, using 14.4 parts of dodecyl sodium sulfate. The white solid product contains 73.8% S. (theory 68.8). The corresponding solid products are obtained when poly-beta-acryloyloxyethylmethacrylammonium methyl sulfate and poly-beta-ethacryloyloxyethylmethacrylammonium methyl sulfate are used as starting material.

Nylon and polycrylonitrile fabrics treated with these products, according to Example IX, show marked anti-static properties which are durable to washing.

Example XI

Example IX when repeated, using 17.2 parts of n-hexadecyl sodium sulfate in 450 parts of water, yields the corresponding polymeric ammonium hexadecenyl sulfate salt, which contains 5.97% S. (theory 6.15). This white salt shows marked anti-static properties and durability to washing when applied to fabrics as described in Example IX.

Example XII

Poly-beta-methacryloyloxyethyltrimethyl ammonium octyl sulfate is prepared by the procedure of Example IX, using 11.3 parts of the corresponding polymeric methyl sulfate salt in 126 parts of water. The white solid contains 8.99% S. (theory 8.40). When applied to nylon and polycrylonitrile from a 2% alcoholic solution, it gives good anti-static properties and durability to washing.

References Cited in the file of this patent

UNITED STATES PATENTS