LUBRICATING, ANTISTAT AND DYE LEVELING AGENT AND PROCESS FOR TEXTILE MATERIALS

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1,970,578 8/1934 Schoeller ................. 8/93
3,399,953 9/1968 Sapers................... 8/93
3,685,956 8/1972 Raal et al. .............. 8/177 AP

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ABSTRACT

Both polycrylonitrile and cationic dyeable polyester fibers and yarns are dyed with cationic dyes in the presence of an agent which operates as a leveling, lubricating and antistatic agent. Dyeings of excellent levelness are obtained, and there is a high uniformity of distribution of lubricating and antistatic agent on the fibers and yarns. The agent comprises (a) 30 to 80 parts of a quaternary ammonium compound having the formula:

\[
\begin{align*}
\text{R}_2 & \quad \text{N}^+ \quad \text{R}_3 \\
\text{R}_1 & \quad \text{X}^- \\
\text{R}_4 & \\
\end{align*}
\]

where \( R_1 \) is a benzyl group or an alkyl group containing 1 to 14 carbon atoms, \( R_2 \) is a benzyl group or an alkyl group containing 1 to 14 carbon atoms, \( R_3 \) and \( R_4 \) are alkyl groups containing 1 to 3 carbon atoms and \( X^- \) is a water-solubilizing anion; and (b) 20 to 70 parts of a polyoxyethylene compound having the formula:

\[
\begin{align*}
\text{CH}_2 & \quad \text{R}_1 \\
\text{CH}_2 & \quad \text{R}_1 \\
\text{CH}_2 & \quad \text{R}_1 \\
\text{O} & \quad \text{X}^- \\
\end{align*}
\]

where \( n \) in an integer of about 6 to 15, \( R_5 \) and \( R_6 \) are etherifying or esterifying moieties of aliphatic alcohols containing 10 to 20 carbon atoms, aliphatic acids containing 10 to 20 carbon atoms or alkyl phenols of the type having the formula:

where \( R_7 \) is an alkyl group containing 8 to 12 carbon atoms. When either \( R_5 \) or \( R_6 \) is an alkyl phenol, the other moiety must be an aliphatic acid or an aliphatic alcohol.

16 Claims, No Drawings
This invention relates in general to a process and composition for treating polyacrylonitrile and cationic dyeable polyester textile materials, and more specifically, to a process for applying a dye leveling, lubricating and antistatic agent to polyacrylonitrile and cationic dyeable polyester materials and compositions therefor.

Polyacrylonitrile and polyester polymers and blends thereof with other synthetic or natural textile materials hereinafter referred to as polyacrylonitrile and polyester textile materials are widely used in the production of textile products such as, knitted garments, carpeting, furnishings, and the like. The polyacrylonitrile and polyester polymers used in these applications have excellent physical and aesthetic properties. The conversion of fabrics and yarns of polyacrylonitrile or polyester polymers into the acrylic or polyester fabrics suitable for these applications or into the finished garment itself, requires two basic processing steps, namely, coloration of the fiber or yarn by dyeing to provide aesthetic appeal and knitting or weaving of the yarn into fabrics or garments.

In dyeing the polyacrylonitrile or polyester textile materials in certain cases the fibers are dyed in stock form followed by spinning into the yarn before conversion into fabrics or finished textile products. The required processes of conversion in such a case are dyeing, spinning, and knitting, weaving or tufting. In general, the dyeing process precedes the spinning process (as in stock dyeing), but it may also follow the spinning process, e.g., as in yarn dyeing.

In the dyeing of the polyacrylonitrile polymers used in textile production the dyeing process is greatly enhanced by incorporating anionic groups into the polymer chains by a copolymerization process during the synthesis of the poly-acrylonitrile polymers. These anionic groups permit the fibers to be dyed by both cationic (basic) and disperse dyes in acid dye baths. This invention applies to all such polyacrylonitrile materials which are modified with an adjuvants which provide anionic dye sites as acceptors for cationic dyestuffs as well as to those which are not modified.

Polyacrylonitrile fibers and yarns are most commonly dyed with the cationic dyes because they give rapid dyeing of the polyacrylonitrile fibers to deep and bright shades due to the strong affinity of the fibers for cationic dyes. However, due to the rapid rate of exhaustion of the cationic dyes onto the polyacrylonitrile fibers and due to the non-uniformity in the distribution on the polymer chains of the anionic groups with which the cationic dyes react, level dyeings are difficult to obtain. One method well-known in the art, of overcoming this difficulty is to dye the acrylics in the presence of cationic quaternary ammonium compounds, such as, benzyl trimethyl ammonium chloride and the like. These cationic agents redistribute the dye where uneven exhaustion of dye onto the fiber has taken place, thereby equalizing the amount of dye attached to the fibers having higher and lower amounts of anionic groups. Thus, it is generally necessary to treat the polyacrylonitrile fibers with a dye leveling agent. The dye leveling agents are generally added to the dyebath solution but may be added to the fibers before they are treated in the dyebath solution.

After the polymer has been dyed, the spinning and/or knitting process is carried out with the dyed yarn or fiber stock. In both of these cases the fiber must be treated with a lubricating agent which reduces the fiber/metal and fiber/fiber coefficients of friction to allow the mechanical processes of spinning and knitting to take place smoothly and without interruption. The most common cause of breakage of fibers or yarns is excessive friction development during the process. This is overcome by the application of a lubricant or lubricating agent. A properly functioning lubricating agent also permits easy slippage of fibers over each other while still maintaining good cohesion of the fibers to produce a strong yarn. The lubricants also must possess antistatic properties to prevent buildup of static electricity during the process. The polyacrylonitrile and polyester textile materials which are dyed with cationic dyes.

The production of textiles based upon polyacrylonitrile and polyesters fibers requires the use of chemical additives to achieve level dyeing, suitable lubrication and antistatic protection. The leveling agent is generally added to the dyebath. The lubricant and antistatic agents are generally added prior to or during the mechanical processes of spinning and knitting. For spinning stock the lubricant and antistatic agent are usually applied by spraying the stock before spinning, a procedure which results in a non-uniform distribution of the lubricating and antistatic agents on the stock. The knitting lubricants are applied directly to the yarn during the rewinding process, also with problems of uniform distribution. Non-uniformity of lubricant and antistatic agents on the fibers and yarns presents serious problems, e.g., breakage, in the spinning and knitting operations. In addition to the non-uniformity the application of lubricants and antistatics to the fibers and yarns by these methods add an additional step to the total process of conversion of fiber to textile product. This additional step increases costs, in terms of material, time and labor. Elimination of a separate lubricant-antistatic agent treatment step or steps would lead to a desirable advantage in economy. The development of a method of uniform application would lead to a desirable technical advantage.

Attempts have been made in prior art processes and compositions to eliminate the multiple steps of applying antistatic agent, lubricating agent and/or dye leveling agent, e.g., by applying them to the dyebath or by applying them in a bath separate from the dyebath. However, most of these attempts have failed due to the interference of the agents with the dyeing of the textiles, the formation of precipitates in the dyebath, or failure to produce the three properties desired, that is, dye leveling, lubricating and antistatic effects.

In U.S. Pat. No. 3,519,562 Lanner discloses a lubricant composition of a wax in combination with a cationic quaternary ammonium emulsifier and an optional non-ionic emulsifier. The emulsifiers are used therein to provide stability against separation of the ingredients of the composition. The lubricant properties are derived from the wax portion of the composition. The Lanner composition is not applied in conjunction with a dyebath composition. According to Lanner the
agent may be applied to acrylics and has utility for the pickling, carding, spinning, plying, twisting, winding, weaving, knitting, napping, and calendaring processes, but its value for promoting leveling of dyeing and antistatic properties to acrylics is doubtful especially in view of the fact that cationic emulsifiers are of the class which comprise quaternary ammonium compounds with alkyl groups having as many as 20 carbon atoms. The members of this class of quaternary ammonium compounds operate as dye retarders rather than as dye migrating agents, and are not useful in producing level dyeings in medium and dark shades on polycrylonitrile textile material, since they seriously reduce the amount of dye that is exhausted from the dyebath onto the fiber. In addition, the composition of Lanner tends to increase, rather than decrease, the build-up of electrostatic charge on the fiber since the wax part of the composition is an insulating agent. Covering fibers with a film of such material therefore decreases the electrical conductivity of the fiber, and accordingly, decreases the ability of the fiber to discharge electrostatic charges built up on the fiber to the surrounding atmosphere.

Compositions containing leuco vat dyestuff, about 4-8 percent (by weight) of a water-soluble non-ionic surface active agent containing a poloxyethylene chain and derived from a compound containing at least 10 carbon atoms and a reactive hydrogen atom, and about 0.4-1.5 percent (by weight) of a water-soluble cationic surface active quaternary ammonium compound containing an aliphatic radical of from 8-18 carbon atoms is disclosed by Mautner et al in U.S. Pat. No. 2,992,062 for the dyeing of polycrylonitrile. The Mautner et al composition which is predominately non-ionic surface active agent with minor amounts of cationic surface active agent operates as a dye leveling agent in conjunction with vat dyes and reduces friction. However, the class of cationic surface active agents (particularly those having aliphatic radicals containing more than 15 carbon atoms) and the low concentrations thereof as disclosed by Mautner et al is inoperative in dyeing with cationic dyestuffs.

A composition comprising a cationic surfactant, an anionic surfactant and a non-ionic surfactant has been applied to hydrophobic fibers, such as nylon, by Brunt et al in British Pat. No. 873,214. The agent comprising the three types of surfactants, has been found useful as a detergent and an antistat on the hydrophobic fibers and is not used in conjunction with the dyeing process. Brunt et al disclose a composition comprising 88.3 percent octadecydienyl trimethyl ammonium chloride and octadecenyl-trimethyl ammonium chloride cationic surface active agent and 11.7 percent of p-dodecylphenyl polyethylene glycol ether containing 17 ethylene glycol residues, having inferior electrostatic properties as well as inadequate detergency power, the only Brunt et al embodiment having cationic surface active agent and non-ionic surface active agent. It comprises a very high concentration of cationic surface active agent relative to the concentration of the non-ionic surface active agent. Brunt et al. do not provide in a single agent a lubricant, dye leveling agent and antistat. Furthermore, the Brunt et al. agent is not applied in a dyebath composition.

OBJECTS OF THE INVENTION

Accordingly, it is an object of this invention to provide a process for applying a suitable agent to polycrylonitrile textile or polyester materials for improving lubricating and antistatic properties of the textile materials without interfering with the dyeing of the textile material.

It is another object of this invention to provide a composition for imparting lubricating and antistatic properties to polycrylonitrile and polyester textile materials said composition also acting as a dye leveling agent.

Another object of this invention is to provide a composition and process for uniformly applying to a polycrylonitrile or polyester textile, materials having lubricating, antistatic and dye leveling properties.

Still another object of this invention is to provide a composition and process to eliminate separate process steps for the application of antistats, lubricants, and dye leveling agents to polycrylonitrile and cationic dyable polyester textile materials.

Another object of this invention is to provide a process and composition of matter for applying a lubricating agent, an antistatic agent and a dye leveling agent simultaneously to a polycrylonitrile and polyester textile material without affecting the leveling and brightness of the dye applied to said material and without causing precipitation or flocculation of dyebath ingredients.

Other objects will become evident to those skilled in the art from a reading of this specification and the appended claims.

SUMMARY OF THE INVENTION

We have found that these and other objects are accomplished by using a quaternary ammonium compound and a poloxyethylene compound in a dyebath for dyeing polycrylonitrile textile materials. A synergetic effect is produced when about 30 to 80 parts (by weight) of the quaternary ammonium compounds of this invention and about 20 to 70 parts (by weight) of the poloxyethylene compounds of this invention (parts by weight express the relationship of the compounds to each other) are added to an acid dyebath containing at least one cationic dye, and we have found that these materials not only have a leveling effect upon the dyeing of polycrylonitrile and cationic dyable polyester textile materials, but also result in a substantial reduction of friction and static in the textile material. Thus, the dyebath composition of this invention provides in a single composition a dye leveling agent, a lubricating agent and an antistatic agent for both polycrylonitrile and cationic dyable polyester textile materials.

By cationic dyable polyester we mean those fibers comprising copolymers of poly(ethylene terephthalate) and sulfonated poly-(ethylene terephthalate) and textile materials prepared therefrom. Textile materials as used herein refers to polycrylonitrile textile materials and cationic dyable textile materials.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred composition of this invention comprises about 30 to about 80 parts of a quaternary ammonium compound having the formula:
where R₁ is a benzyl group or an alkyl group containing about 1 to about 14 carbon atoms, R₃ is a benzyl group or an alkyl group containing about 1 to about 14 carbon atoms, R₄ and R₅ are alkyl groups containing about 1 to about 3 carbon atoms and X⁻ is a water-solubilizing anion; and about 20 to about 70 parts of a polyoxyethylene compound having the formula:

\[
\begin{align*}
\text{CH}_2-\text{R}_3 & \quad \text{X}^- \\
\text{CH}_2-\text{R}_4 & \quad \text{X}^- \\
\end{align*}
\]

where n is an integer of about 6 to about 15, R₁ and R₄ are etherifying or esterifying moieties selected from the group consisting of aliphatic alcohols containing about 10 to about 20 carbon atoms, aliphatic acids containing about 10 to about 20 carbon atoms, alkyl phenols of the type having the formula:

\[
\begin{align*}
\text{R}_2 & \quad \text{OH} \\
\end{align*}
\]

where R₂ is an alkyl group containing about 8 to about 12 carbon atoms and mixtures thereof, in an aqueous acid dyebath solution suitable for dyeing polyacrylonitrile or cationic dyeable polyester textile materials and containing at least one cationic dye. Parts by weight of quaternary ammonium compound and the polyoxyethylene compound expresses the relationship of said quaternary ammonium compounds to said polyoxyethylene compound and may be about 30 to about 80 parts by weight quaternary ammonium compound to about 20 to about 70 parts by weight polyoxyethylene compound. When either R₃ or R₅ is an alkylphenol, the other moiety (R₄ or R₅) must be the aliphatic alcohol, the aliphatic acid or mixtures thereof.

As used herein the quaternary ammonium compound and the polyoxyethylene compound may be added separately to the dyebath solution or may be combined within the designated ratios and thereafter added to the dyebath solution. The quaternary ammonium compounds of the present invention are preferably salts of benzyl, dibenzyl, benzylalkyl or alkyl ammonium compounds. Examples of the alkyl radicals, R₁ and R₃ having from about 1 to about 14 carbon atoms in the generic formula of the quaternary ammonium compound, are methyl, ethyl, propyl, isopropyl, butyl, dodecyl, lauryl, myristyl and the like and mixtures thereof. Examples of the alkyl radicals containing about 1 to 3 carbon atoms and represented by R₄ and R₅ in the generic formula of the quaternary ammonium compound, are methyl, ethyl, propyl, isopropyl and mixtures thereof. The water-solubilizing anion designated by X⁻ in the formula of the quaternary ammonium compound may be any anion which will render the quaternary ammonium compound water-soluble. Examples of such anions are chloride, ethosulfate, bromide, sulfate, acetate, hydroxyacetate, tartrate, gluconate, hydroxide, methosulfate, and the like and mixtures thereof.

Typical quaternary ammonium compounds found useful in the present invention and falling within the generic formula designated above are benzyltrimethylammonium chloride, dibenzylidimethylammonium chloride, lauryltrimethylammonium chloride, dilauryldimethylammonium chloride, benzylidilauryltrimethylammonium chloride, lauryldimethylammonium ethosulfate, myristyltrimethyl ammonium bromide, benzyltriethyl ammonium sulfate, cocotrimethyl ammonium acetate, and the like and mixtures thereof.

The polyoxyethylene compounds found useful in the present invention and falling within the generic formula shown above are characterized by about 6 to 15 ethylene oxide groups linked in a polymer chain and mixtures thereof. The polyoxyethylene compound is also characterized by the presence of etherifying or esterifying groups or mixtures thereof which are derived from aliphatic alcohols containing about 10 to 20 carbon atoms, aliphatic acids containing about 10 to 20 carbon atoms, alkyl phenols of the type:

\[
\begin{align*}
\text{R}_2 & \quad \text{OH} \\
\end{align*}
\]

where R₂ is an alkyl group containing about 8 to 12 carbon atoms, and mixtures thereof, said groups being designated as R₄ and R₅ in the generic formula shown above for the polyoxyethylene compound. When R₄ is an alkyl phenol, R₅ must be an aliphatic alcohol or an aliphatic acid, and conversely when R₅ is an alkyl phenol, R₄ must be an aliphatic alcohol or an aliphatic acid. By etherifying group or moiety we mean the radical of the designated aliphatic alcohols or alkyl phenols which react with the ethylene oxide moieties to form an ether or ether-type linkage. Esterifying groups or moieties are the radicals of the aliphatic carboxylic acids which react with the ethylene oxide units of the polyoxyethylene compound thereby forming ester linkages.

Examples of aliphatic alcohols containing about 10 to 20 carbon atoms are decyl alcohol, isodecyl alcohol, lauryl alcohol, stearyl alcohol, myristyl alcohol, 2, 6, 8-trimethyl-4-nonanol, tridecyl alcohol, oleyl alcohol, cetyl alcohol, arachidic alcohol, tallow alcohol, hexadecyl alcohol, and the like and mixtures thereof. Examples of aliphatic acids containing about 10 to 20 carbon atoms are oleic acid, capric acid, lauric acid, myristic acid, stearic acid, isostearic acid, and the like and mixtures thereof. Examples of alkyl phenols of the type having the formula designated above where R₂ is an alkyl group containing about 8 to 12 carbon atoms, are isooctyl phenol, nonyl phenol, dodecyl phenol, and the like and mixtures thereof.

Typical non-ionic polyoxyethylene compounds useful in the present invention are fatty acid diesters of polymerized glycols having molecular weights ranging from about 250 to 800, fatty acid esters of ethoxylated alcohols and alkyl phenols, and alkyl ethers of ethoxylated alcohol and alkyl phenols. These include the coconut fatty acid diester of polyethylene glycols having 6 to 15 ethylene oxide units, such as polyethylene glycols of molecular weight 400 or 600, the oleic acid diesters of the polyethylene glycols having molecular weights of
about 400 or 600, the oleic acid monoester of ethoxylated (9 ethylene oxide units) isocyanolphenol, the capric acid monoester of ethoxylated (12 ethylene oxide units) tridecyl alcohol, the isodecyl ether of ethoxylated (15 ethylene oxide units) lauryl alcohol.

The amount of quaternary ammonium compound and polyoxyethylene compound added to the dyebath composition may be varied according to the nature of the polyacrylonitrile or polyester textile material and the amount of dyestuff to be applied. In general, about 0.33 percent to about 2.0 percent of the quaternary ammonium compound and about 0.33 percent to about 2.0 percent of the polyoxyethylene compound (based upon the weight of the textile material) is the optimum amount of material which should be added to the dyebath medium. Thus, when the quaternary ammonium compound and the polyoxyethylene compound are mixed before addition to the dyebath medium, it is preferred that about 0.6 percent to about 4.0 percent (based upon fiber or yarn weight) should be added to the dyebath medium. The minimum concentration of quaternary ammonium compound or polyoxyethylene compound is about 0.20 percent (based on fiber weight) of each compound and the maximum concentration of each of the compounds which may be added to the dyebath medium is about 3.0 percent (based upon fiber weight). In general, the minimum concentration of either the polyoxyethylene compound or the quaternary ammonium compound which may be used in the present invention, is contingent upon that quantity of the compounds which will produce adequate lubrication, reduction of static electricity and dyestuff leveling, and quantities of less than 0.20 percent (based upon fiber weight) of each of the compounds is generally inadequate for lubrication, antistatic performance and dye leveling. Accordingly, a sufficient amount of the polyoxyethylene compound and the quaternary ammonium compound must be used to provide adequate lubrication, antistatic performance and dyestuff leveling. Generally, if amounts greater than 3.0 percent (based upon fiber weight) of polyoxyethylene compound is used there is a tendency toward poor crock fastness and soiling characteristics, and if amounts of quaternary ammonium compound in excess of 3.0 percent (based upon fiber weight) are used there is a tendency toward loss of color yield. Generally, heavier dyings can be made with a smaller amount of the quaternary ammonium additive, and lighter shades are obtained with larger amounts of the quaternary ammonium compound. One skilled in the art can determine suitable concentrations of the quaternary ammonium compound and the polyoxyethylene compound in relation to fiber weight.

In the dyeing of the polyacrylonitrile and cationic dyebale polyester textile materials in accordance with this invention, it is preferred that the textile material be in the form of either stock fiber or the yarn produced from spinning the stock fiber, however, a textile fabric woven from the yarn may also be dyed in accordance with the present invention, and fabric so dyed will be characterized by having a reduced friction and increased antistatic properties. The textile material is retained within the dyebath composition of this invention until the material has been dyed to a suitable shade. The dyebath composition may be heated after the textile material is added thereto, or the bath may be heated when the material is introduced therein. It is deemed within the purview of one skilled in the art to adjust the temperature of the dyebath. Generally the textile materials are held at the boil, approximately 212°F., for about 40 minutes. After dyeing, the fiber or yarn may be rinsed briefly to remove only excess dyestuff and chemicals without the loss of the antistatic and lubricant additives.

Other chemical additives are ordinarily employed in the dyeing of the textile materials. For example, acetic acid and sodium acetate are used as buffers to maintain pH control of the dyebath at between 3.0 and 6.5, the optimum pH for the dyeing of the textile material being about 4.5 to 5.5 for most cationic dyes. Accordingly, the dyebath composition of this invention is designated as an acid dyebath.

Mixtures of the quaternary ammonium compounds and mixtures of the polyoxyethylene compounds of the present invention may be added to the dyebath composition, and accordingly, the quaternary ammonium compound of the present composition may comprise a mixture of said compounds, and the polyoxyethylene compound of the present composition may comprise a mixture of polyoxyethylene compounds.

The dyebath composition of the present invention is a fluid medium and is preferably an aqueous medium in which all ingredients are dissolved and/or in the form of an emulsion. It is generally preferred that the composition of the present invention contain no solid material. The polyoxyethylene compounds useful in the present invention are water-soluble or emulsifiable, and the quaternary ammonium compounds are salts which are also soluble or emulsifiable in water. Accordingly, the quaternary ammonium compounds and the non-ionic polyoxyethylene compounds of the present invention can be added to the dyebath composition in an aqueous system in the form of a solution or an emulsion.

Although one skilled in the art can determine the solids to liquor ratio (polyacrylonitrile or polyester textile material to dyebath), it is preferred that the solids to liquor ratio be about 1 part (by weight) polyacrylonitrile to about 20 parts (by weight) dyebath liquor, or generally within the range of about 1 to 10 parts textile material to about 1 to 40 parts dyebath liquor.

The present invention applies only to the dyeing of polyacrylonitrile and cationic dyeable polyester textile materials with cationic dyes. A single cationic dye or a mixture of cationic dyes may be applied to the textile material. Typical cationic (basic) dyes which may be used in the present invention are Basic Yellow 12, C.I. 48,065, Basic Orange 21, C.I. 48,035, Basic Violet 10, C.I. 45,170, Basic Yellow 11, C.I. 48,055, Basic Green 4, C.I. 42,000, Basic Violet 3, C.I. 42,555, and the like. The cationic dyes are normally soluble in water and are completely dissolved in the fluid medium of the present composition and process. The amount of cationic dyes used in the dyebath composition may be determined by one skilled in the art. The amount of dye may vary according to the particular dye or mixture of dyes used and the desired depth of shade of the resulting material.

The following examples are set forth to illustrate more clearly the principles and practice of the invention to those skilled in the art. In the examples given below all chemical concentrations are expressed as percent of polyacrylonitrile fiber, yarn, or fabric weight unless otherwise specified.
EXAMPLES

EXAMPLE 1

An aqueous dyebath was prepared by mixing 1 percent Basic Yellow 11, C.I. No. 48,055, 10 percent Glaubers salt, 2 percent acetic acid, 1 percent sodium acetate and additive as designated in Table I below. The percentages are based on weight of fiber. Polyacrylonitrile yarn (Orlon) in cone form was dyed at 212°F. for 40 minutes in a liquor to polyacrylonitrile ratio of 20:1 with the above solution in a dyeing apparatus (Gaston County Package Dyeing Machine). After dyeing, the yarn was rinsed for 5 minutes at 120°F. The cone of yarn was dried and conditioned overnight at 30 percent relative humidity at 70°F. before testing. The following tests were run:

Co-efficient of friction of the yarn against ceramic was measured on a Rothschild F Meter at a yarn speed of 100 meters per minute and an initial tension of 20 grams.

Static buildup on the yarn was measured on a Rothschild Static Voltmeter after 3 minutes running under the conditions given above.

Cohesion of the fibers was measured by determining the maximum speed of winding on a Rothschild Friction Tester at maximum tension before breakage occurred.

The leveling power of the migrating/lubricating composition was determined by knitting the undyed yarn into a sleeve of fabric. A portion of this knitted fabric was dyed with 2 percent (based on weight of goods) Basic Blue 3, C.I. No. 51,005, and dried. A portion of the dyed fabric and an equal weight of undyed fabric were immersed in 20 times their combined weight of solution, containing 4 percent additive, 10 percent Glaubers salt, and 2 percent acetic acid (percentages expressed on weight of goods). The goods were treated in the boiling solution in a dyeing apparatus (Ahiba Vistamatic Dyeing Machine). After rinsing and drying, the degree of dye transfer from dyed to undyed fabric was rated visually. In the table below under the column heading "Relative Dye Migrating Efficiency", 1 designates the greatest degree of dye migration and represents the best dye migrating efficiency.

In the art satisfactory lubrication and antistatic performance is achieved when the coefficient of friction is less than 0.40 and the voltage buildup is less than 450 volts.

The results obtained are shown in Table I:

**TABLE I**

<table>
<thead>
<tr>
<th>Additive</th>
<th>Coefficient of friction</th>
<th>Voltage before buildup (volts)</th>
<th>Yarn speed before breakage (meters/minute)</th>
<th>Relative dye migrating efficiency 1=best</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original yarn*</td>
<td>0.42</td>
<td>5,000</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>No dye, no additive.</td>
<td>0.33</td>
<td>3,000</td>
<td>26</td>
<td>2</td>
</tr>
<tr>
<td>4% quaternary A</td>
<td>0.48</td>
<td>2,000</td>
<td>42</td>
<td>2</td>
</tr>
<tr>
<td>4% ester A</td>
<td>0.33</td>
<td>1,800</td>
<td>90</td>
<td>2</td>
</tr>
<tr>
<td>4% blend C</td>
<td>0.31</td>
<td>200</td>
<td>120</td>
<td>1</td>
</tr>
</tbody>
</table>

1 Quaternary A = A 60 percent aqueous solution of benzyltrimethylammonium chloride.
2 Ester B = The coconut fatty acid ester of ethoxylated nonylphenol, containing 10 units ethylene oxide.
3 Blend C = An aqueous blend containing 70 parts (by weight) of Quaternary A and 30 parts (by weight) of Ester B.
4 No dye, no additive. **Dyed, no additive.**

EXAMPLE 2

The dyeing procedure of Example 1 was repeated using as additives, 1.67 percent benzyltrimethylammonium chloride and 1.2 percent oleic acid diester of polyethylene glycol 400, based upon fiber weight. The coefficient of friction was 0.31 and the voltage was 350 volts. The dyeing was perfectly level. When ethoxylated nonylphenol containing 10 ethylene oxide units was used in place of the oleic acid diester (not in accordance with this invention) the coefficient of friction was 0.53 and the voltage was 750 volts.

EXAMPLE 3

The dyeing procedure of Example 1 was repeated using as additives, 1.67 percent lauryltrimethylammonium chloride and 4 percent Ester B of Example 1. The coefficient of friction was 0.28 and the voltage was 150 volts.

EXAMPLE 4

The dyeing procedure of Example 1 was repeated using as additives, 1.67 percent cocobenzyl dimethyammonium chloride and 4 percent Ester B of Example 1. The coefficient of friction was 0.32 and the voltage was 55 volts.

EXAMPLE 5

The dyeing procedure of Example 1 was repeated using as additives, 1.7 percent dibenzyl dimethyammonium chloride and 4 percent Ester B. The coefficient of friction was 0.31 and the voltage was 50 volts.

EXAMPLE 6

The dyeing procedure of Example 1 was repeated using as additives, 1.67 percent dilauryldimethylam-
3,773,463

EXAMPLE 7

The dyeing procedure of Example 6 was repeated replacing the Ester B with ethoxylated nonylphenol containing 10 ethylene oxide units, which is not in accordance with this invention. A coefficient of friction of 0.53 and a voltage build-up of 1,200 volts was obtained. Thus, the lubricating and antistatic properties of the yarn treated in accordance with this invention were not satisfactory.

In accordance with the above examples, the objects of this invention have been carried out. The process and dyebath composition of the present invention produce level dyeings and at the same time impart to the dye fibers lubricating and antistatic properties suitable for the mechanical operations of spinning and/or knitting which follow the dyeing procedure. Three highly desirable objectives have been accomplished by our invention, namely, dyeing of excellent leveling is obtained; a high uniformity of distribution of lubricating and antistatic properties on the fibers or yarns is obtained due to the fact that the leveling/lubricating agent is applied to the fiber by exhaustion during the course of the dyeing; and application of lubricating and antistatic agent during the dyeing process eliminates the need for a separate lubricant/antistat application step prior to the mechanical processing of the dyed fiber or yarn.

The above examples are not meant to limit the scope of the invention or the application to which this invention may be directed. It is to be understood that although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited, since changes and alterations therein may be made which are in the full intended scope of this invention as defined by the appended claims.

We claim:
1. A composition for simultaneously dyeing, lubricating and applying an antistat to textile materials consisting of:
   a. a fluid medium;
   b. at least one cationic dye;
   c. a quaternary ammonium compound having the formula:

\[
\begin{align*}
R_1 & \quad \text{alkyl radical, alkyl radical and mixtures thereof, said alkyl radical containing about 1 to about 14 carbon atoms;} \\
R_2 & \quad \text{alkyl radical, alkyl radical and mixtures thereof, said alkyl radical containing about 1 to about 14 carbon atoms;}
\end{align*}
\]

where \( R_1 \) is selected from the group consisting of benzyl radical, alkyl radical and mixtures thereof, said alkyl radical containing about 1 to about 14 carbon atoms; \( R_2 \) is selected from the group consisting of benzyl radical, alkyl radical and mixtures thereof, said alkyl radical containing about 1 to about 14 carbon atoms; \( R_3 \) and \( R_4 \) are alkyl radicals containing about 1 to about 3 carbon atoms and \( X^- \) is a water-solubilizing anion; and

\[
\begin{align*}
\text{a polyoxyethylene compound having the formula:}
\end{align*}
\]

where \( R_5 \) is an alkyl group containing about 8 to about 12 carbon atoms, and mixtures thereof, at least one of the \( R_3 \) and \( R_4 \) moieties being selected from the group consisting of aliphatic alcohols containing about 10 to about 20 carbon atoms, aliphatic acids containing about 10 to about 20 carbon atoms, alkylphenols of the type having the formula:

\[
\begin{align*}
\text{where } n & \text{ is an integer of about 6 to 15, } R_5 \text{ and } R_6 \text{ are etherifying and esterifying moieties selected from the group consisting of aliphatic alcohols containing about 10 to about 20 carbon atoms, aliphatic acids containing about 10 to about 20 carbon atoms, alkylphenols of the type having the formula:}
\end{align*}
\]

2. The composition of claim 1 wherein said quaternary ammonium compound is selected from the group consisting of benzyltrimethyl ammonium chloride, dibenzyltrimethyl ammonium chloride, lauryltrimethyl ammonium chloride, dilauryltrimethyl ammonium chloride, benzyllauryltrimethyl ammonium chloride, lauryldimethyl ethyl ammonium ethosulfate, myristyltrimethyl ammonium bromide, benzyltriethyl ammonium sulfate, cocotrithemyl ammonium acetate, and mixtures thereof.

3. The composition of claim 1 wherein said polyoxyethylene compound is selected from the group consisting of fatty acid diesters of polymerized glycols having molecular weights ranging from about 250 to 800, fatty acid esters of ethoxylated alcohols, fatty acid esters of ethoxylated alkylphenols, alkyl ethers of ethoxylated alcohols, alkyl ethers of ethoxylated alkylphenols, and mixtures thereof.

4. The composition of claim 3 wherein the fatty acid diester of polymerized glycol is selected from the group consisting of the coconut fatty acid diester of polyethylene glycol having 6 to 15 ethylene oxide units, and the oleic acid diester of polyethylene glycol having 6 to 15 ethylene oxide units; the fatty acid ester of ethoxylated alcohol is the capric acid monoester of ethoxylated tridecyl alcohol having 12 ethylene oxide units; the fatty acid ester of ethoxylated alkylphenol is the oleic acid monoester of ethoxylated isooctyl alcohol having 9 ethylene oxide units; and the alkyl ether of ethoxylated alcohol is the isodecyl ether of ethoxylated lauryl alcohol having 15 ethylene oxide units.

5. The composition according to claim 1 wherein the total concentration of quaternary ammonium compound and polyoxyethylene compound is about 0.2 percent to about 6 percent (by weight) based on the weight of the material to be dyed.

6. The composition of claim 1 for simultaneously dyeing, lubricating and applying antistat to polyacrylonitrile textile materials.
7. The composition of claim 1 for simultaneously dyeing, lubricating and applying an antistatic to cationic dyeable polyester textile materials.

8. A process for level dyeing textile materials with cationic dyes and simultaneously applying a lubricating and antistatic agent thereinto comprising:
   a. adding to an acid dyebath having at least one cationic dye, at least one quaternary ammonium compound having the formula:

   \[
   \begin{array}{c}
   R_2 \\
   R_7 - N - R_3 \\
   R_4 \\
   \end{array}
   \]

   where \( R_i \) is selected from the group consisting of benzyl radical, alkyl radical and mixtures thereof, said alkyl radical containing about 1 to about 14 carbon atoms; \( R_4 \) is selected from the group consisting of benzyl radical, alkyl radical and mixtures thereof, said alkyl radical containing about 1 to about 14 carbon atoms; \( R_3 \) and \( R_4 \) are alkyl radicals containing about 1 to about 3 carbon atoms and \( X^- \) is a water-solubilizing anion; and at least one polyoxyethylene compound having the formula:

   \[
   \begin{array}{c}
   \text{CH}_2 \\
   \text{CH}_2 \\
   \text{CH}_2 \\
   \text{O} \\
   \end{array}
   \]

   where \( n \) is an integer of about 6 to 15, \( R_3 \) and \( R_4 \) are etherifying and esterifying moieties selected from the group consisting of aliphatic alcohols containing about 10 to about 20 carbon atoms, aliphatic acids containing about 10 to about 20 carbon atoms, alkylphenols of the type having the formula:

   \[
   \begin{array}{c}
   \text{O} \\
   \text{R}_7 \\
   \end{array}
   \]

   where \( R_7 \) is an alkyl group containing about 8 to about 12 carbon atoms, and mixtures thereof, at least one of the \( R_3 \) and \( R_4 \) moieties being selected from the group consisting of the aliphatic acid, aliphatic alcohol and mixtures thereof when the other \( R_3 \) and \( R_4 \) moiety is an alkylphenol, the ratio of said quaternary ammonium compound to said polyoxyethylene being about 30 to about 80 parts by weight quaternary ammonium compound to about 20 to about 70 parts by weight polyoxyethylene compound;

   b. adding the textile material to said dyebath;
   c. heating said dyebath; and
   d. removing the textile material from said dyebath.

9. A process in accordance with claim 8 wherein said quaternary ammonium compound is selected from the group consisting of benzyltrimethyl ammonium chloride, dibenzylmethyl ammonium chloride, lauryltrimethyl ammonium chloride, dialkyldimethyl ammonium chloride, benzylauridimethyl ammonium chloride, lauryldimethylthethyl ammonium ethosulfate, myristyltrimethyl ammonium bromide, benzyltriethyl ammonium sulfate, cocotrimethyl ammonium acetate and mixtures thereof.

10. A process in accordance with claim 9 wherein said polyoxyethylene compound is selected from the group consisting of fatty acid diesters of polymerized glycols having molecular weights ranging from about 250 to 800, fatty acid esters of ethoxylated alcohols, fatty acid esters of ethoxylated alkylphenols, alkyldiethers of ethoxylated alcohols, alkyl ethers of ethoxylated alkylphenols and mixtures thereof.

11. A process in accordance with claim 10 wherein the fatty acid diester of polymerized glycol is selected from the group consisting of the coconut fatty acid diester of polyethylene glycol having about 6 to about 15 ethylene oxide units, and the oleic acid diester of polyethylene glycol having about 6 to about 15 ethylene oxide units; the fatty acid ester of ethoxylated alcohol is the capric acid monoester of ethoxylated tridecyl alcohol having 12 ethylene oxide units; the fatty acid ester of ethoxylated alkylphenol is the oleic acid monoester of ethoxylated isoctylphenol having 9 ethylene oxide units; and the alkyl ether of ethoxylated alcohol is the isodecyl ether of ethoxylated lauryl alcohol having 15 ethylene oxide units.

12. A process in accordance with claim 8 wherein the total concentration of quaternary ammonium compound and polyoxyethylene compound is about 0.2 percent to about 0.6 percent (by weight) based on the weight of the material to be dyed.

13. The process of claim 8 wherein the textile material is stock fiber.

14. The process of claim 8 wherein the textile material is yarn.

15. The process of claim 8 wherein the textile material comprises a polycryliclonitrile.

16. The process of claim 8 wherein the textile material comprises a cationic dyeable polyester.