Films and fibers having modified ion affinity and hydrophilicity produced through reaction of such substrates with polyoxyalkylene polyaziridines

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ABSTRACT OF THE DISCLOSURE

Antistatic properties can be imparted to synthetic hydrophobic materials, cellulosic materials, and blends of cellulosic materials with synthetic, hydrophobic materials by contacting said materials with a selected polyaziridine compound.

This application is a continuation application of Ser. No. 183,050 filed Mar. 28, 1962, now abandoned, which is relied on.

This invention relates to a process for imparting valuable properties to natural and synthetic materials and to the materials thus formed. This invention further relates to a process for imparting durable antistatic properties to hydrophobic materials and, more particularly, to a process for imparting antistatic properties to shaped synthetic hydrophobic materials such as films, fibers, yarns, fabrics, and the like, and to the antistatic materials thus formed. This invention also relates to a process for imparting dimensional stability and affinity for dyestuffs to natural fibers and shaped hydrophobic materials containing natural fibers.

As more and more uses are found for synthetic materials in the form of films, fibers, yarns, textiles, etc., it is noted that many of these materials have hydrophobic properties and thus have a detrimental tendency to accumulate static electrical charges. The continuously expanding use of these synthetic hydrophobic materials in the manufacture of all types of garments, curtains, drapes, upholstery, automobile seat covers, and the like, to mention merely a few fields, results in the demand for increasingly better methods for effectively eliminating the accumulation of static electrical charges on the shaped materials. Furthermore, during the processing and manufacture of textiles from such synthetic, hydrophobic materials, the accumulation of static electrical charges on the fibers and yarns interferes with the spinning, weaving, knitting, etc., operations, it causes materials to attract lint and soil, and renders more difficult the cutting and sewing operations. The accumulation of static electricity during the processing of yarns and fibers to form fabrics may also cause spark discharges which constitute a significant hazard in the textile industry. When the textiles are in the form of garments, the presence of the static electrical charges thereon is objectionable in use, since they cause the garment to cling uncomfortably to the wearer.

Many attempts have been made to obviate the aforesaid disadvantages and prevent the accumulation of static electricity on hydrophobic synthetic materials by treating these materials with certain chemical compounds, commonly referred to as anti-static agents or finishes. Many of these known antistatic agents, however, are susceptible to removal during the laundering or dry cleaning of the textile, and sometimes even by mere rinsing of the textile in water. To obviate this disadvantage, durable antistatic agents have been developed and found effective, but even these still have certain objectionable features. Many of the more durable antistatic agents must be applied under strongly alkaline conditions in order to achieve the desired results in the finishing treatment, thereby leading to a lack of compatibility with many other commonly used functional finishes. In many instances, undesirable features are obtained during the finishing process, one of which is the discoloration of the finished textile. Furthermore, many of these more durable antistatic agents must be used with a curing agent, which usually must be present in a critical ratio relative to the treating solution, thus leading to a limited bath stability and to difficulties in controlling the finishing process. Many of these known durable antistatic agents can be cured only at elevated temperatures, thus making them unsuitable for use with synthetic hydrophobic fibers having low softening points.

Accordingly, it is an object of the present invention to obviate the aforesaid disadvantages presently existing with known antistatic agents for hydrophobic materials, and with the processes utilizing such agents for imparting antistatic properties to hydrophobic materials, including obviating the use of alkaline catalysts or the addition of curing agents as additional reactive components in the treating baths.

It is another object of this invention to provide a process for imparting to hydrophobic materials the property of readily dissipating electrostatic charges normally formed thereon.

It is a further object of this invention to provide a durable finish on a synthetic hydrophobic material which enables the materials to retain moisture and to possess a high degree of conductance.

It is still another object of this invention to provide a shaped structure of synthetic material in which the accumulation of static electrical charges is effectively eliminated due to the presence of an antistatic finish thereon, which finish is durable and thus not readily removed by repeated launderings and dry cleanings, and which finish does not impair the properties of the shaped structure with regard to its appearance, hand, color, strength, abrasion resistance, and the like.

Another object of this invention is to provide a process for improving the affinity of hydrophobic synthetic materials, including polyolefin fibers, for acid dyestuffs.

It is also a further object of this invention to provide a process for improving the affinity of cellulosic materials and materials containing cellulosic fibers for acid dyestuffs, and the product thus formed.

It is a further object of this invention to provide an i on-exchange resin and, further, a process for making the aforesaid resin.

In attaining the objects of this invention, one feature resides in contacting the material whose properties are to be modified with a solution, dispersion, or emulsion containing a sufficient amount of a monomer of the in-
vention and insolubilizing the monomer, in situ, on the material to form the desired finish on the material.

Other objects, features, and advantages of the invention will be more apparent from the following discussion thereof.

It has been discovered that many properties of materials including hydrophobic synthetic materials, materials containing natural fibers, such as cellulose fibers, and even cellulosic materials, per se, such as cotton textiles, may be vastly improved by treating the material with a compound having the formula

\[
\begin{align*}
R & \quad C \\
R & \quad (X)_1-\cdots-(R'\Omega)-R-(Y) \quad N \\
& \quad C \\
& \quad R'
\end{align*}
\]

wherein

- \( R, R', R'' \) are members selected from the group consisting of hydrogen and lower alkyl, and
- \( R' \) is an alkylene radical having from 2 to 3 carbon atoms,
- \( X \) and \( Y \) are divalent organic radicals, \( n \) is an integer selected from the group consisting of 1 and 0, and
- \( m \) is an integer from 3–50 inclusive.

While reference is made to the lower alkyl radicals, good results are obtained when the length of the carbon chain is from 1 to 6 carbons, and best results are obtained when the lower alkyl radical has from 1 to 4 carbon atoms. While compounds wherein \( R, R', R'' \) may have more than 6 carbon atoms will perform satisfactorily, it is difficult to obtain such compounds commercially at this time.

The preparation of compounds wherein \( n = 0 \), which are among the preferred compounds for the present invention, is discussed in copending application Ser. No. 94,720 filed Mar. 10, 1961, now U.S. Pat. No. 3,197,463, and the disclosure of said application relating to the compounds and to the preparation thereof is expressly incorporated herein. Compounds wherein \( n = 1,0 \), and \( X \) and/or \( Y \) are defined by the radical \(-OCOR^3-\) where \( R^3 \) is a low molecular weight, aliphatic hydrocarbon radical, as disclosed in U.S. Pat. 2,596,200, and all references to these compounds are incorporated herein.

For the purposes of the present invention the divalent organic radical \( X \) and \( Y \) in the above formula may also include the following groups:

- \(-OCOR^4-, \quad -OSO_2R^5-, \quad -SO_2R^6-, \quad -NHCOR^6-, \quad -\text{NHSO}_2R^7-, \quad \text{and the like.}\)

Examples of compounds wherein \( X \) and \( Y \) are present in the formula (n=1) and have the aforesaid definitions are as follows:

1. \(-OCOR^4-\); products of reaction of imines with bis acrylates, bis methacrylates and bis crotonates of polyoxyalkylene glycols, as described in U.S. Pat. 2,596,200.

2. \(-OSO_2R^6-\); products of reaction of imines and diesters of polyoxyalkylene glycols with substituted and unsubstituted vinyl sulfonic acids.

3. \(-SO_2R^6-\); products of reaction of imines with bis vinyl sulfonyl or with bis haloalkyl sulfonyl compounds.

4. \(-NHSCR^4-\); products of reaction of imines with bis acrylamides, methacrylamides, and crotonamides, which are prepared by acylation of polyoxyalkylene amines with carboxylic acid chlorides.

5. \(-\text{NHSO}_2R^7-\); products of reaction of imines with bis acrylamides, methacrylamides, and crotonamides, which are prepared by acylation of polyoxyalkylene amines with sulfonic acid chlorides.

Other definitions of \(-X- \) and \(-Y-\), wherein the compounds of the above formula will perform satisfactorily will be readily apparent and thus, the nature of the divalent organic groups \(-X- \) and \(-Y-\) is not critical for the purpose of the invention, although aliphatic divalent organic groups are preferred.

Compounds of the above formula polymerize on heating to form the novel cross-linked polymeric products on the synthetic hydrophobic materials, which products are capable of retaining moisture and possess a high degree of conductance.

The essentially monomeric compounds are applied in the form of a solution, emulsion, or dispersion, and the polymerization and insolubilization thereof occur in situ on the treated material.

For the specific purpose of improving the properties of textile materials manufactured from hydrophobic fibers, and preventing the accumulation of static electrical charges thereon, the monomeric compounds of the aforesaid generic formula are applied from solution, dispersion, or emulsion, by impregnation, spraying, or by other known methods, and the treated textile is then reacted to achieve polymerization and insolubilization of the compound applied. The amount of the monomer required to impart satisfactory properties, and, more specifically, durable antistatic properties, is preferably from between 0.2% to 10%, based on the weight of the textile. It will be appreciated that while more than 10% of the agent can be applied, no appreciable improvements are to be noted, and, in fact, the polymerized product may have undesirable properties, such as tackiness, when present in excessive amounts. After application of the antistatic agent, the textile is preferably heated to accelerate the polymerization process. While the reaction proceeds slowly at room temperature, its rate increases with a corresponding increase in the temperature.

If desired, rapid reactions can be achieved even at room temperature or below, by the addition of known acidic or acid-forming, catalysts or alkylating agents which greatly accelerate the polymerization reaction and insolubilization of the monomer. Acid or acid-forming catalysts are numerous and may include non-volatile mineral acids, such as \( \text{H}_2\text{SO}_4 \), hydrochlorides, sulfates, nitrates, etc., of weak organic bases; chlorides and nitrates of magnesium and zinc; acid sulfates and phosphates of alkali metal; and other suitable compounds. Generally speaking, the amount of the compound and the reaction conditions resulting in optimum properties and performance of the treated material depend to a considerable extent on the chemical and physical structure of the hydrophobic substrate employed, and can be readily determined. The amount of polymer remaining in the finished product is generally between 50 and 100% of the amount applied, and a polymer content of 0.1% to 10% in the finished product, based upon the weight of the material treated, is preferred.

Included among the synthetic hydrophobic materials which exhibit improved properties when treated according to the process of the present invention are polyamide fibers (commonly referred to as nylon), polyester fibers (which include those sold under the trademark Dacron by E. I. du Pont de Nemours & Co.), polyolefin fibers, acrylic fibers, acrylonitrile fibers (which include those sold under the trademark Orlon by E. I. du Pont de Nemours & Co.), cellulose triacetate fibers, polyethylene terephthalate yarns, and the like. Such hydrophobic structures are more fully defined in U.S. Patent 2,982,751 and the definition thereof is incorporated herein by reference. Mixtures or blends of hydrophobic fibers with natural fibers also exhibit greatly improved properties when treated according to the process of the present invention and, in some instances, highly desirable results are achieved by employing the process to simultaneously impart antistatic properties to the synthetic hydrophobic fiber component and other desirable
properties, such as enhanced dyeability and dimensional stability, to the natural fiber component, such as the cellulosic fiber component. Thus, when a polyester-wool blend fabric is treated by the process of the invention, the end product is rendered durably antistatic and dimensionally stable. When a polyester-cellulose blend fabric is treated by the process of the invention, durable antistatic properties are imparted to the polyester portion of the fabric, while dimensional stability and increased dyeability with acid dyes are achieved with respect to the cellulosic portion of the fabric.

When hydrophilic substrates such as cellulose or those containing cellulosic polymers, including cotton, rayon, paper, wood, linen, etc., are treated in accordance with the invention, the monomer is converted to the polymer which, it is believed, becomes attached to the cellulose molecules by chemical bonds and enormously increases the dyeability of the cellulosic substrate with acid dyes. However, applicant does not wish to be bound by any theory as to why the unexpected results are obtained.

Furthermore, the polymerization reaction of the monomers can be carried out in bulk, independently of the presence of any substrate, and the polymerization products which are formed have utility as ion-exchange materials in other processes, when prepared either in the absence of a substrate or in the presence of an inorganic carrier such as silica gel.

The effectiveness of the new finishes on synthetic hydrophobic materials is evaluated by known test procedures. For example, resistivity of an untreated hydrophobic material is generally extremely high and, in the case of fabrics manufactured from hydrophobic fibers, it is known that a specific area resistivity higher than $10^{12}$ ohms at 40% relative humidity indicates a high tendency to the accumulation of static charges. Test methods for measuring resistivity in textiles are described in several publications, including the Technical Manual of the American Association for Textile Chemists and Colorists, vol. 35, pp. 138–139, Method Nos. Standard 76–1939 (Fabrics) and Tentative 84–1955 (Yarns). The resistivity results reported in the following examples were obtained by the test methods cited above.

The resistance of the finish to laundering and dry cleaning was evaluated by measuring the resistivity of the treated samples by standard methods after repeated washings or dry cleanings. The following examples are merely illustrative of the invention, and are not to be considered limiting the scope of the invention in any manner. All parts are by weight unless otherwise specified.

**EXAMPLE 1**

A swatch of undyed, bleached taffeta fabric woven from 100% Dacron polyester yarn was impregnated on a laboratory paddle with an aqueous solution containing 60 grams per liter of the following monomer,

\[ CH_3 \text{N} \left(\text{CH}_{2} \text{CH}_3 \text{CH} \text{O})_2\text{CH}_2\text{CH}_2\text{N} \right] \text{H} \]

at a wet pickup of 33%, thus depositing 2% monomer on the weight of the fabric. The sample was dried, heated for 2 minutes at 300° F. and rinsed. The fabric so treated had a specific area resistivity (SAR) of $5 \times 10^4$ ohms (at 70° F. and 40% RH as specified in the test method used), whereas the untreated fabric had a specific area resistivity higher than $10^9$ ohms. Even after 5 machine launderings at 140° F., the treated fabric had a specific area resistivity (SAR) of $3 \times 10^9$ ohms, showing even less tendency to static accumulation than fabrics woven from hydrophilic fibers such as cotton and rayon fabrics which exhibit a SAR of the order of $10^8$ ohms.

**EXAMPLE II**

The procedure of Example I was repeated, except that 20 grams per liter of magnesium chloride were added to the treating solution. The SAR of the treated fabric was $1.1 \times 10^8$ ohms after the heating step, $2.4 \times 10^9$ ohms after one laundering and $9 \times 10^9$ ohms after 5 machine launderings at 140° F.

**EXAMPLE III**

The procedure of Example I was repeated, except that the fabric used was pretreated with a 1% aqueous solution of sulfuric acid and dried prior to impregnation with the monomer solution. After impregnation, the treated fabric was dried at 220° F. and allowed to stand at room temperature for 24 hours. The SAR of this treated fabric was $4 \times 10^9$ ohms. After one laundering it was $1.2 \times 10^{10}$ ohms and after 5 dry cleaning treatments it was $9 \times 10^9$ ohms.

**EXAMPLE IV**

Four swatches of undyed bleached Dacron polyester fabric were impregnated on a laboratory paddle with an aqueous solution containing 50 grams per liter of the following monomer:

\[ CH_3 \text{N} \left(\text{CH}_{2} \text{CH}_3 \text{CH} \text{O})_2\text{CH}_2\text{CH}_2\text{N} \right] \text{H} \]

at a wet pickup of 35% thus yielding 1.75% of the monomer on the weight of the fabric. The swatches were dried at 250° F. and then the polymerization reaction of the monomer on the fabric was allowed to take place under varying conditions of time and temperature. The samples were then rinsed. The SAR values obtained on these samples (measured at 40% RH and 70° F.) after treatment, and after various laundering and dry cleaning procedures, are tabulated below:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Reaction</th>
<th>Temperature</th>
<th>As treated</th>
<th>After 5 launderings</th>
<th>After 10 dry cleanings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated fabric</td>
<td>1 hr.</td>
<td>Room temp.</td>
<td>$&gt;10^9$</td>
<td>$&gt;10^9$</td>
<td>$&gt;10^9$</td>
</tr>
<tr>
<td>2</td>
<td>30 sec.</td>
<td>300° F.</td>
<td>$1.5 \times 10^9$</td>
<td>$6 \times 10^9$</td>
<td>$7 \times 10^9$</td>
</tr>
<tr>
<td>3</td>
<td>3 min.</td>
<td>SAC F.</td>
<td>$1.7 \times 10^9$</td>
<td>$3 \times 10^9$</td>
<td>$7 \times 10^9$</td>
</tr>
<tr>
<td>4</td>
<td>1 wk.</td>
<td>Room temp.</td>
<td>$1.3 \times 10^9$</td>
<td>$6 \times 10^9$</td>
<td>$8 \times 10^9$</td>
</tr>
</tbody>
</table>

It is apparent from these results that the insolubilization reaction proceeds very slowly at room temperature and that the finish is removed in laundering from sample 1. Sufficient time at room temperature (sample 2), or a short time at elevated temperature (samples 3 and 4) cause the polymerization reaction to proceed to an adequate extent, thereby insolubilizing the finish and making it resistant to laundering and dry cleaning. The following Example V will demonstrate the accelerating effect of magnesium chloride upon the polymerization reaction.

**EXAMPLE V**

The procedure of Example IV was repeated, except that 50 grams per liter of magnesium chloride hexahydrate were added to the treating solution. The SAR val-
ues obtained on the samples so treated are tabulated below:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Reaction time</th>
<th>Temperature</th>
<th>As treated</th>
<th>After 5 launderings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated fabric</td>
<td>1 hr</td>
<td>Room temp.</td>
<td>&gt;10^3</td>
<td>&gt;10^3</td>
</tr>
<tr>
<td>6</td>
<td>1 wk</td>
<td>60 °C</td>
<td>1.0x10^4</td>
<td>6x10^3</td>
</tr>
<tr>
<td>7</td>
<td>30 sec</td>
<td>300 °F</td>
<td>1.0x10^4</td>
<td>5x10^3</td>
</tr>
<tr>
<td>8</td>
<td>3 min</td>
<td>300 °F</td>
<td>1.1x10^3</td>
<td>2.2x10^3</td>
</tr>
</tbody>
</table>

It is apparent that outstanding resistance to static accumulation can be obtained by these processes, and that the finished fabric product maintains its antistatic properties even after repeated laundering. It has also been found that the antistatic properties of the finished fabric are maintained even after dry cleaning treatments.

**EXAMPLE VI**

Three swatches of scoured, heat set, dyed nylon tricot fabric were impregnated on a laboratory padder with an aqueous solution containing 25 grams per liter of the monomer represented by the formula shown in Example IV. The wet pickup was 80% yielding 2% of the monomer on the weight of the fabric. The swatches were dried at 280 °F, then heat or cured at 310 °F for varying times to induce polymerization of the monomer applied. The samples were then rinsed. The SAR values obtained on the nylon tricot samples so treated are tabulated below:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Reaction time at 300 °F</th>
<th>SAR, ohms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated fabric</td>
<td>&gt;10^3</td>
<td>&gt;10^3</td>
</tr>
<tr>
<td>9</td>
<td>2 min</td>
<td>1.0x10^4</td>
</tr>
<tr>
<td>10</td>
<td>6 min</td>
<td>3.3x10^3</td>
</tr>
</tbody>
</table>

It is apparent that the 2 minute reaction time is sufficient to achieve insolubilization and durability of the finish. The reaction can be accelerated by the addition of acidic or acid-forming catalysts to the treating solution.

**EXAMPLE VII**

Similar results were obtained when the procedure of Examples IV, V, and VI were repeated using the compound

\[
\text{CH}_2-N\text{CHCH}_3\text{CH}_2\text{CH}_2\text{N}_3\text{CH}_3\text{CH}_3
\]

**EXAMPLE VIII**

Samples of dyed, scoured fabric woven from 100% spun Orion yarn (a polymer of acrylonitrile) were impregnated on a laboratory padder with the following aqueous solutions containing the compound:

\[
\text{CH}_2-N\text{CHCH}_3\text{CH}_2\text{CH}_2\text{N}_3\text{CH}_3\text{CH}_3
\]

**TABLE 4**

<table>
<thead>
<tr>
<th>Solution:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
</tbody>
</table>

The wet pickup for this fabric under the padding conditions used was approximately 80%. The padded samples were dried, then divided in several portions in order to establish the optimum reaction conditions. Portions of each sample were reacted under the following conditions:

(a) at room temperature for 24 hours
(b) at 280 °C for 3 minutes
(c) at 300 °F for 5 minutes

After the reaction period, the samples were rinsed. All samples so treated exhibited excellent antistatic properties (SAR of the order of 10^8 ohms or lower at 40% RH and 70 °F.) and the antistatic properties were still excellent after 30 machine launderings at 140 °F.

**EXAMPLE IX**

A swatch of undyed bleached polyester fabric was treated on a laboratory padder with an aqueous solution containing 50 grams per liter of the compound:

\[
\text{CH}_2-N\text{CHCH}_3\text{CH}_2\text{CH}_2\text{NCHCH}_3\text{CH}_3\text{CH}_3
\]

at 35% wet pickup. The treated fabric sample was dried, then heat for 5 minutes at 300 °F to induce polymerization of the monomer applied, and rinsed. The SAR of the cured fabric was 1.6x10^11 ohms as treated, and 6x10^11 after laundering at 140 °F.

**EXAMPLE X**

Samples of a polyester/wool fabric woven from yarns consisting of 55% polyester fiber and 45% wool fiber were treated with the compound of the formula shown in Example I from aqueous solutions containing 20, 40, 60, and 80 grams per liter of the compound and containing 5, 10, 15, and 20 grams per liter respectively of magnesium chloride hexahydrate. The padded samples were dried and cured for 5 minutes at 300 °F and rinsed. They were then compared with the untreated control fabric in tests for tendency to accumulate static electricity (SAR value—test method I.c.) and for dimensional stability (test method, Technical Manual of the American Association of Textile Chemists and Colorists, vol. 35, p. 133, test No. 1).

**TABLE 5**

<table>
<thead>
<tr>
<th>Monomer conc. in solution</th>
<th>As treated</th>
<th>After 1 laundering</th>
<th>After 5 launderings</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 g/liter</td>
<td>1.6x10^10</td>
<td>5x10^8</td>
<td>1.5</td>
</tr>
<tr>
<td>60 g/liter</td>
<td>2.2x10^10</td>
<td>6x10^8</td>
<td>2.0</td>
</tr>
<tr>
<td>40 g/liter</td>
<td>3.3x10^10</td>
<td>7x10^8</td>
<td>3.0</td>
</tr>
<tr>
<td>20 g/liter</td>
<td>4.5x10^10</td>
<td>7x10^8</td>
<td>5.0</td>
</tr>
<tr>
<td>Untreated fabric</td>
<td>&gt;10^13</td>
<td>&gt;10^13</td>
<td>7.5</td>
</tr>
</tbody>
</table>
The results tabulated above demonstrate the outstanding combination of properties, namely antistatic properties and dimensional stability, which can be achieved on polyester/wool blend fabrics by the use of the new process. Treatment of a 70/30 polyester/wool blend fabric also yielded a product of excellent properties.

**EXAMPLE XI**

A fabric woven from 100% polypropylene spun yarn was treated on a laboratory padder with an aqueous solution containing 100 grams/liter of the compound represented by the formula shown in Example VIII and 20 grams/liter of magnesium chloride hexahydrate. The wet pickup was 60%, and the amount of monomer deposited on the fabric was 6% based on the weight of the fabric. The treated fabric was heated for 30 minutes at 200°F. and rinsed. The finished fabric exhibited excellent antistatic properties. When the fabric was dyed by conventional procedures with acid dyestuffs (including Acid Red 106, Acid Blue 23, and the like), the polymers formed on the fabric acquired a deep shade which was resistant to washing. Both antistatic properties and affinity for acid dyestuffs were maintained through repeated launderings and dry cleanings. Untreated polypropylene exhibits an extreme tendency to static accumulation and no affinity for acid dyes.

**EXAMPLE XII**

A bleached, desized cotton fabric was padded with a solution containing 35 grams/liter of the compound represented by the formula shown in Example VIII and 10 g./liter of zinc fluoroborate, dried, cured for 30 minutes at 200°F. and rinsed. The cotton fabric so treated was dyed a deep bright shade with the following dyestuffs: Acid Yellow 23, Acid Blue 23, Acid Yellow 65, Acid Violet 34, and Acid Orange 74. The color imparted was fast to washing, and treated fabric which had been washed even repeatedly, maintained affinity for the acid dyes, while untreated cotton fabric could not be dyed under comparable conditions.

The dyestuffs referred to in the foregoing examples are identified by the following numbers in the Color Index, American Association of Textile Chemists & Colorists, second edition, 1956:

- Acid Yellow 23—New C.I. No. 19140
- Acid Blue 23—New C.I. No. 61125
- Acid Yellow 65—New C.I. No. 13095
- Acid Violet 34—New C.I. No. 61710
- Acid Orange 74—New C.I. No. 18745
- Acid Red 106—New C.I. No. 18110

Application of the antistatic finish of the present invention may be made to any form of the shaped structure including foams, fabric, yarn, tow, staple, films, plastic sheeting, and the like.

Many modifications of the above examples will be apparent to those skilled in the art without departing from the basic concept of the invention.

I claim:

1. A material selected from the group consisting of a synthetic, hydrophobic material unblended with proteinaceous fibers, a cellulose textile material, and a blend of a synthetic, hydrophobic textile material and a cellulose textile material, said material having a finish thereon of a polymerized and insolubilized monomer represented by the formula

\[
\begin{align*}
N-\left(\text{CH}_{2}\text{CH}_{2}\text{O}\right)_{m}-\text{CH}_{2}\text{CH}_{2}\text{NH-CH}_{2}\text{CH}_{2}\text{N}
\end{align*}
\]

wherein

- R, R' and R'' are hydrogen or lower alkyl,
- R'' is an alkylene radical having 2 or 3 carbon atoms,
- and \( m \) is an integer from 3 to 50, inclusive, or

2. A product as set forth in claim 1 wherein said material is a synthetic, hydrophobic textile material.

3. A product as set forth in claim 1 wherein said material is in film form.

4. A product as set forth in claim 2 wherein said textile is formed from polypropylene.

5. A product as set forth in claim 2 wherein said textile is formed from a polymer of acrylonitrile.

6. A product as set forth in claim 2 wherein said textile is formed from a polyamide.

7. A product as set forth in claim 2 wherein said textile is formed from a polyester.

8. A product as set forth in claim 1 wherein said material is a cellulosic textile material.

9. A product as set forth in claim 1 wherein said material is a blend of a synthetic, hydrophobic textile and a cellulosic textile material.

10. A synthetic hydrophobic material unblended with proteinaceous fibers, as set forth in claim 1 having a finish thereon of a polymerized and insolubilized monomer of the formula

\[
\begin{align*}
N-\left(\text{CH}_{2}\text{CH}_{2}\text{O}\right)_{m}-\text{CH}_{2}\text{CH}_{2}\text{NH-CH}_{2}\text{CH}_{2}\text{N}
\end{align*}
\]

said finish imparting antistatic properties to said synthetic hydrophobic material.

11. A synthetic hydrophobic material unblended with proteinaceous fibers, as set forth in claim 1 having a finish thereon of a polymerized and insolubilized monomer of the formula

\[
\begin{align*}
N-\left(\text{CH}_{2}\text{CH}_{2}\text{O}\right)_{m}-\text{CH}_{2}\text{CH}_{2}\text{NH-CH}_{2}\text{CH}_{2}\text{N}
\end{align*}
\]

said finish imparting antistatic properties to said synthetic hydrophobic material.

12. A synthetic hydrophobic material unblended with proteinaceous fibers, as set forth in claim 1 having a finish thereon of a polymerized and insolubilized monomer of the formula

\[
\begin{align*}
N-\left(\text{CH}_{2}\text{CH}_{2}\text{O}\right)_{m}-\text{CH}_{2}\text{CH}_{2}\text{NH-CH}_{2}\text{CH}_{2}\text{N}
\end{align*}
\]

said finish imparting antistatic properties to said synthetic hydrophobic material.

13. A synthetic hydrophobic material unblended with proteinaceous fibers, as set forth in claim 1 having a finish thereon of a polymerized and insolubilized monomer of the formula

\[
\begin{align*}
N-\left(\text{CH}_{2}\text{CH}_{2}\text{O}\right)_{m}-\text{CH}_{2}\text{CH}_{2}\text{NH-CH}_{2}\text{CH}_{2}\text{N}
\end{align*}
\]

said finish imparting antistatic properties to said synthetic hydrophobic material.

14. A synthetic hydrophobic material unblended with proteinaceous fibers, as set forth in claim 1 having a
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11. The process as set forth in claim 10 wherein said synthetic hydrophobic material is in film form.

12. The process as set forth in claim 15 wherein said synthetic hydrophobic material is in film form.

13. A process for imparting desirable properties to a material selected from the group consisting of a synthetic hydrophobic material unblended with proteinaceous fibers, a cellulosic textile material and a blend of a synthetic hydrophobic textile material and a cellulosic textile material comprising applying to said material in an amount sufficient to impart said properties of a monomer represented by the formula

\[
\begin{align*}
\text{CH}_2-\text{CH} \\
\text{N-CH-CH}_2\text{COO-} \\
\text{CH}_3 \\
\text{CH}_3
\end{align*}
\]

15. A process for imparting desirable properties to a material selected from the group consisting of a synthetic hydrophobic material unblended with proteinaceous fibers, a cellulosic textile material and a blend of a synthetic hydrophobic textile material and a cellulosic textile material comprising applying to said material in an amount sufficient to impart said properties of a monomer represented by the formula

\[
\begin{align*}
\text{CH}_2-\text{CH} \\
\text{N-CH-CH}_2\text{COO-} \\
\text{CH}_3 \\
\text{CH}_3
\end{align*}
\]

16. The process as set forth in claim 15 wherein said material is a synthetic hydrophobic textile material unblended with proteinaceous fibers.

References Cited

UNITED STATES PATENTS

3,197,463 7/1965 Tesoro et al.

GEORGE F. LESMES, Primary Examiner

J. CANNON, Assistant Examiner

U.S. Cl. X.R.

8—115.5, 116.2, 100, 168, 54.2, 55; 117—155, 143, 139.5, 138.8; 260—2.1, 9, 13, 857, 860, 897, 898, 899
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Column 9, beginning at line 66 in formula (1) the structure should be as follows:

\[
\begin{align*}
R & \quad R^1 \\
N & \quad C \\
C & \quad R^2 \\
H & 
\end{align*}
\]

Signed and sealed this 25th day of June 1974.

(SEAL)
Attest:
EDWARD M. PLETCHER, JR.  
Attesting Officer
C. MARSHALL DANN  
Commissioner of Patents