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PROCESS OF AND COMPOSITION FOR PRODUCING IMPROVED TEXTILE MATERIALS HAVING OIL AND WATER REPELLENT AND ANTISTATIC PROPERTIES

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The present invention relates to a novel process for imparting durable water repellent and antistatic properties in a single operation to textile materials manufactured from hydrophobic fibers. More specifically the present invention relates to a novel process for imparting water repellent, oil repellent, and antistatic properties to textile materials and fabrics manufactured wholly or in part from hydrophobic synthetic fibers.

Many products and processes are known which may be used to render textiles or fabrics water repellent, and some are known to impart properties which are resistant to laundering and dry cleaning. There are also many known products and processes which are claimed to impart antistatic properties to hydrophobic textile materials. Some of the known antistatic finishes also withstand repeated launderings and drycleaning. However, the combination of durable water repellent and durable antistatic properties for hydrophobic fibers has not been possible heretofore. In fact, even very recently, experiments[1] conducted "by simultaneously applying the water repellent and certain antistatic finishes, which are compatible in the treating bath, have shown that both the water repellency and the static propensity suffer in degree of effectiveness." Thus, even in those instances in which there appears to be compatability of antistatic finishes with other functional finishes, in the bath, each combination represents a special study, and there appears to be no fixed rules to guide the experimenter.

In the foregoing connection hydrophobic fibers are defined as synthetic fibers such as polyamide fibers, polyvinyl chloride fibers, triacetate fibers, acrylic fibers, polyester fibers and the like, which have a comparatively low capacity to retain moisture in comparison with such fibers as cotton, wool and rayon. Textile materials prepared from these hydrophobic fibers accumulate electrostatic charges when exposed to rubbing during processing or in use, and the use of suitable antistatic finishes is necessary in order to reduce or overcome the objectionable tendency to static accumulation. On the other hand, water repellent properties are essential when synthetic fibers are employed in the manufacture of fabrics which are to be exposed to rain and snow.

The imparting of water repellent and antistatic properties to a given fabric, however desirable, would appear to be unattainable since the effectiveness of an antistatic finish depends in large measure on its affinity for water while the effectiveness of a water repellent finish depends on its lack of affinity for water. It is known, for example, that a water repellent finish can lose its effectiveness completely when contaminated by ionic impurities, such as residual detergent particles from wash or drycleaning solutions. For this reason the combination of a water repellent finish with a hydroscopic, ionic, antistatic finishing agent would be expected to lead to the complete loss of the water repellent properties, or of the antistatic properties, or possibly both. The Army Quartermaster Report cited above lends support to this theory. Accordingly, it would be highly beneficial to

[1] Measuring and Predicting the Generation of Static Electricity in Military Clothing, Textile Series, Report No. 110, Hqtrs., Quartermaster Research and Engineering Center, U.S. Army, Natick, Mass. (September 1959).

the textile industry to provide a process for imparting both water repellent and antistatic properties to hydrophobic fibers in a single treatment.

It is, therefore, an object of the present invention to provide a novel process whereby hydrophobic textile materials are simultaneously provided with water repellent, oil repellent and antistatic properties.

It is a further object of this invention to provide a novel process whereby these desirable properties are imparted to the textile materials by a single treatment.

It is a further object of this invention to provide a novel composition which imparts water and oil repellent plus antistatic properties to hydrophobic textile materials.

It is a further object of this invention to provide a novel process whereby the aforementioned water repellent, oil repellent and antistatic properties imparted to the textile materials are durable to repeated laundering and drycleaning cycles.

It is a further object of this invention to provide textile materials which exhibit satisfactory durable water repellency, oil repellency and antistatic properties without impairment of their appearance, hand, strength or physical properties generally.

Other objects and advantages of the invention will be apparent from the description which follows.

The novel process of the present invention comprises impregnating hydrophobic synthetic fibers with an aqueous solution, dispersion or emulsion containing:

(*a*) An oil and water repelling fluorochemical compound;

(*b*) A cationic polyelectrolyte; and

(*c*) A curing agent designed to crosslink and insolubilize the cationic polymer, thus rendering it durable to washing.

The fluorochemical compounds, which are used to impart water and oil repellent properties, can have chemical structures that vary widely. For example, acrylates and methacrylate of hydroxyl compounds containing a highly fluorinated residue and their polymers and copolymers can be used. Fluorochemical compounds of this type are defined with greater particularity in U.S. Patents 2,642,416; 2,826,564; 2,839,513; 2,803,615. Other fluorochemical compounds which can be employed as oil-and-water repellent agents include the chromium cordination complexes of saturated perfluoromonocarboxylic acids of which the chromium complexes of perfluorobutyric acid and perfluorooctanoic acid are presentative.[2] Fluorochemical compounds suitable for the process of our invention are available commercially, for example, those marketed under the trade name of "Scotchgard" by the Minnesota Mining and Manufacturing Company.

The cationic polyelectrolytes, which serve as antistatic agents, can be crosslinked and rendered insoluble (thermoset) by heating in the presence of a suitable curing agent. Their chemical structure can also vary widely. These compounds can be further described as water soluble polymers containing reactive amino groups. Some examples of these polyelectrolytes are described in recent publications and patents.[3] Cationic polyelectrolytes suitable for the process of our invention are available commercially, for example those marketed under the trade name "Aston" by the Onyx Chemical Co. of Jersey City, N.J.

The curing agents contemplated are polyfunctional alkylating agents, capable of reacting with the polyamine antistatic agent, rendering it insoluble and thus resistant to washing and drycleaning. The polyfunctional halides (ref. 3(*a*) supra) and polyfunctional epoxides are examples of curing agents which can be usefully employed

[2] Textile Res. J. 28, 233–241 (1958).

[3] (*a*) Textile Res. J. 29, 21–31 (1959), (*b*) U.S. Patent 2,882,185, (*c*) U.S. Patent 2,914,427, (*d*) British Patent 797,175.

in the process of our invention. Polyepoxides are available commercially under various trade names, for example Eponite 100 (a product of the Shell Chemical Corp.), Kopoxite 159 (a product of Koppers Company, Inc.) and many others. Polyepoxides are generally prepared by the reaction of aliphatic or aromatic polyhydroxyl compounds with epichlorohydrin, followed by dehydrohalogenation of the resulting poly-chlorohydrin. Among polyfunctional halides, the polyethylene glycol diiodides are preferred because of their high reactivity and solubility properties. A representative of this group is, for example, the compound known as "Aston Catalyst" which is a product of the Onyx Chemical Co. of Jersey City, New Jersey, and which is a polyoxy alkylene glycol dihalide corresponding to the formula $X(C_nH_{2n}O)_yC_nH_{2n}X$ in which

X is halogen,
n has a value of 2 to 3, and
y has a value of 3 to 30.

The amounts of each material used in the impregnating solution may be varied within wide limits, depending on the type of fabric employed and on the end use requirements for water repellency, oil repellency, static propensity and durability. The following ranges are preferred, and give excellent results on many types of fabrics:

(*a*) 1% to 5% of an aqueous dispersion of a fluorochemical compound (about 30% active ingredient);
(*b*) 2% to 10% of a cationic polyelectrolyte product (containing about 20% active ingredient); and
(*c*) 0.2 to 1.0% of a curing agent.

All percentages are given on the weight of fabric treated. The actual percentage deposited on the fabric in the course of treatment can be calculated from the percent concentration of each material in the treating solution and the percent wet pick-up of the fabric. After impregnation with the solution or emulsion, the textile is passed through the squeeze rolls of a padder or other similar device, dried and heated in a curing oven to bring about polymerization of the resins. The time and temperature of curing may be varied widely. Curing temperatures of 280° F. to 350° F. for 1 minute to 5 minutes give excellent results. After curing, the treated textile can be rinsed or subjected to a mild detergent wash in order to remove soluble residues.

The present invention will be more completely illustrated by the following examples, which are illustrative of the excellent results that can be obtained when fabrics manufactured from hydrophobic fibers are treated according to the process of the invention and which examples are not to be construed as being limitative. All parts are by weight unless otherwise specified.

Example 1

A woven 100% nylon fabric which has been dyed but not finished is impregnated with an aqueous solution containing 20 parts of a polymeric, cationic antistatic agent known as "Aston 123" (product of the Onyx Oil and Chemical Co.), 1.7 parts of a curing agent consisting of "Eponite 100" (product of the Shell Chemical Co.) and 8.6 parts of a fluorocarbon polymer known as "Scotchgard FX–204" (product of the Minnesota Mining and Manufacturing Co.) per 100 parts of solution. Care must be taken to adjust the pH of the Aston 123 to 6.0–7.0 before mixing.

The fabric is then passed through the squeeze rolls of a padder. The wet pick-up of the fabric is 33%, indicating that 6.66% Aston 123, 0.63% Eponite 100 and 2.9% Scotchgard (all as supplied) have been deposited on the fabric in the impregnation step. The fabric is dried, cured 5 minutes at 300° F. and washed at 110°–120° F. in a solution of nonionic detergent. The fabric so treated has excellent water repellent, oil repellent and antistatic properties. The color and feel are not affected by the treatment, and the fabric strength is unimpaired.

Example 2

The procedure of Example 1 is repeated on the same fabric, using 20 parts Aston 108 [4] (at pH 10.0) as the antistatic agent, 1.9 parts of Aston Catalyst [4] as the curing agent, and 8.0 parts of Scotchgard FX–204 [5] per 100 parts of solution as the water repellent agent. Excellent water repellent, oil repellent, and antistatic properties are obtained.

Example 3

The procedure of Example 1 is repeated on the same fabric, using 20 parts Aston 108 [4] (at pH 10.0), 1.9 parts of Aston Catalyst [4] and 9.0 parts of Scotchgard FC–154 [5] as the water repellent agent per 100 parts of solution. The same excellent properties noted in Example 1 above are obtained.

Example 4

A woven dyed 100% polyester fabric (Dacron, a trademark of the E. I. du Pont Corp.), is treated according to the procedure of Example 1 with a solution containing 10 parts Aston 108 [4] (pH 10.0), 1.0 part of Aston Catalyst [4] and 8.6 parts Scotchgard FX–208 [5] as the water repellent agent per 100 parts of solution. Again excellent water repellent, oil repellent, and antistatic properties are obtained.

Example 5

A white 40 denier nylon tricot fabric is treated according to the procedure of Example 1 with a solution containing 13 parts of Aston 123 [4] (pH 7.0), 1.4 parts Eponite 100 [6] and 4.3 parts of Scotchgard FX–204 [5] per 100 parts of solution. The wet pickup of the fabric is 70%. After padding, drying, curing and washing, the fabric has excellent appearance and outstanding properties with respect to being water repellent, oil repellent, and antistatic.

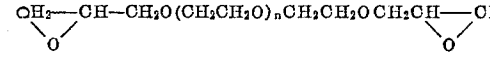
Aston 123 and Aston 108 are polyamines in which the recurring unit can be represented by the formula

$$-N(R)-(C_nH_{2n}O)_yC_nH_{2n}-$$

In this formula

R is a lower alkyl (C_1 to C_3),
n has a value of 2 to 3, and
y has a value of 3 to 30.

For a further description of these polyamines, see U.S. Patent No. 3,021,232. Eponite 100 is a bis-glycidyl ether of a polyethylene glycol and can be represented by the formula



For a further discussion of these compounds see U.S. Patent No. 2,982,751. The Scotchgards are aqueous emulsions of polymers of perfluoroalkyl acrylates. Typical perfluoroalkyl acrylate monomers would be for example

$$CH_2{=}CHCOOCH_2(CF_2)_nCF_3$$

in which n has a value of 2 to 8.

Several tests can be employed to establish the effectiveness of the present process for imparting water repellent, oil repellent, and antistatic properties to synthetic fibers. Some of the accepted test procedures are as follows.

For water repellency:

(*a*) AATCC spray test, Test Method 22–1952. Manual of the American Association of Textile Chemists and Colorists (AATCC), 1959 edition, p. 164.

[4] Product of the Onyx Chemical Co.
[5] Product of Minnesota Mining and Manufacturing Co.
[6] Product of the Shell Chemical Co.

(*b*) Water penetration test, Federal Specification CCC–T–191, Modification POD–112, p. 3.

For static properties (electrical resistivity):

AATCC Test Method 76–1959 (adopted as tentative 76–1954, revised 1958, approved as standard 1959). Manual of the AATCC, 1959 edition, p. 138.

For oil repellency:

Minnesota Mining and Manufacturing Scotchgard technical bulletin, Appendix A.

Durability to laundering:

Test before and after laundering in a home style automatic washer, agitator type, water temperature 140° F., with detergent.

Durability to drycleaning:

Commercial drycleaning, either perchloroethylene or Stoddard solvent.

Accepted standards of performance for treated fabrics by the test methods listed above are—

For water repellency:

(*a*) Spray test—80 or higher.

(*b*) Water penetration—60 minutes or longer.

For electrical resistivity:

5×10^{12} ohms or lower.

For oil repellency:

Spray ratings of 80 or higher.

The test results obtained on the fabrics treated as described in Examples 1–5 are summarized below.

Fabric	Treatment	Water repellency spray rating	Water penetration, time	Oil repellency spray rating	Resistivity ohms at 35% RH [1]
Woven nylon	None (control)	0	0 (immediate)	0	$>10^{13}$
Do	Example 1		Over 120 mins.	100	1×10^{10}
Do	Example 1 after 5L [2]		do	90	1×10^{11}
Do	Example 2		60 mins.	100	3×10^{9}
Do	Example 2 after 5L		30 mins.	90	3×10^{10}
Do	Example 3		Over 120 mins.	100	4×10^{9}
Woven Dacron	None (control)	0	0	0	$>10^{13}$
Do	Example 4	100		80	4×10^{11}
Do	Example 4 after 5 dry cleanings	80		80	4×10^{11}
Nylon tricot	None (control)	0	0	0	$>10^{13}$
Do	Example 5	100		100	6×10^{10}
Do	Example 5 after 5L	80		100	2×10^{12}

[1] RH=relative humidity. [2] L=laundering.

The foregoing experimental data demonstrate that certain water and oil repellent finishes plus antistatic finishes can be simultaneously applied to hydrophobic fibers so as to impart excellent water repellent, oil repellent, and antistatic properties to said fibers and which properties are durable to subsequent laundering and dry cleaning treating.

While the illustrative embodiments of the invention have been described hereinbefore with particularity, it will be understood that various other modifications will be apparent to and can readily be made by those skilled in the art without departing from the scope and spirit of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and description set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention including all features which would be treated as patentable equivalents thereof by those skilled in the art to which the invention pertains.

What I claim is:

1. A process for simultaneously imparting water repellent, oil repellent and antistatic properties to hydrophobic textile materials comprising impregnating said materials with an oil and water repellent selected from the group consisting of (1) acrylates and methacrylates of hydroxyl compounds containing a highly fluorinated residue and their polymers and copolymers and (2) chromium coordination complexes of saturated perfluoromonocarboxylic acids, an antistatic agent comprising a water soluble polymer containing amino groups and a curing agent selected from the group consisting of (1) polyfunctional halides and (2) polyfunctional epoxides, wherein said repellent, antistatic agent, and curing agent are all in an aqueous medium; removing the excess of solution, and thereafter heat curing the solution in the textile materials.

2. The process of claim 1 in which the oil and water repellent, the antistatic agent, and the curing agent are in an aqueous medium selected from the group consisting of an aqueous solution, an aqueous dispersion, and an emulsion.

3. The process of claim 1 in which the heat curing takes place at temperatures from about 280° F. to 350° F. for a period of about 1 to 5 minutes.

4. The process of claim 3 in which the curing agent is a polyfunctional halide.

5. The process of claim 3 in which the curing agent is a dihalide of a polyethylene glycol.

6. The process of claim 3 in which the curing agent is a polyfunctional polyepoxide.

7. The process of claim 1 in which the oil and water repellent consists of the acrylates and methacrylates of hydroxyl compounds containing a highly fluorinated residue and their polymers and copolymers.

8. The process of claim 1 in which the oil and water repellent consists of chromium coordination complexes of perfluoromonocarboxylic acids.

9. Water repellent, oil repellent and antistatic textile materials made by the process of claim 1.

10. The process of claim 1 in which 1% to 5% of the oil and water repellent; 2% to 10% of a cationic polyelectrolyte product as the antistatic agent; and 0.2 to 1.0% of the curing agent are employed in the aqueous medium, said percentages being in terms of the weight of the textile materials treated.

11. A composition for imparting water repellent, oil repellent, and antistatic properties to textile materials consisting of an oil and water repellent selected from the group consisting of (1) acrylates and methacrylates of hydroxyl compounds containing a highly fluorinated residue and their polymers and (2) chromium coordination complexes of saturated perfluoromonocarboxylic acids, an antistatic agent comprising a water soluble polymer containing amino groups and a curing agent selected from the group consisting of (1) polyfunctional halides and (2) polyfunctional polyepoxides, wherein said repellent, antistatic agent, and curing agent are all in an aqueous medium.

References Cited in the file of this patent

UNITED STATES PATENTS

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2,820,719	Trusler et al.	Jan. 21, 1958
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