United States Patent

[11] 3,619,274

72] Inventor **Thomas Jefferson Proffitt, Jr.**
Kinston, N.C.

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73] Assignee **E. I. du Pont de Nemours and Company**
Wilmington, Del.

54] **COATED SYNTHETIC MATERIAL**
1 Claim, No Drawings

52] **U.S. Cl.** **117/138.8,** 117/139.5, 252/8.8, 260/924

51] **Int. Cl.** **D02j 3/18,** C09k 3/16

50] **Field of Search** ..... 117/139.5 R, 139.5 O, 138.8 U, 138.8 N, 138.8 F; 8/115.6; 252/8.8; 260/924, 925

56] **References Cited**

UNITED STATES PATENTS

,677,700	3/1954	Jackson et al.	117/139.50
,056,744	10/1962	Copes et al.	252/8.8
,080,259	3/1963	La Fleur	252/8.8
3,238,277	3/1966	Sigan et al.	260/925

Primary Examiner—William D. Martin
Assistant Examiner—J. E. Miller, Jr.
Attorney—William B. Cridlin, Jr.

ABSTRACT: Improved antistatic protection has been achieved in synthetic fibers, particularly synthetic staple fibers, by treating the fibers with salts of

1. polyoxyethylene or polyoxypropylene amines; and
2. phosphoric acid esters of
a. monohydroxy alkyl alcohols or
b. polyoxy (ethylene or propylene) monoalkyl ethers.

Most synthetic fibers such as polyamide, acrylic and polyester fibers are hydrophobic and tend to develop and retain static charges. Before such fibers can be converted into textiles, it is necessary to apply an antistatic finish. It is most economical to apply such a finish to the fiber at the point of manufacture. This requires application to a large rope of continuous filaments travelling at high speed. A suitable finish must have a low-viscosity and a low-surface tension in solution in order to penetrate the tow rapidly. The finish on the fiber should remain nontacky even when exposed to humid air. If the finish becomes tacky, the fibers cannot be carded and spun into uniform yarns.

COATED SYNTHETIC MATERIAL

The present invention provides compositions which can be easily dispersed in water to yield dispersions of low-viscosity and low-surface tension. The invention also provides compositions which will readily penetrate heavy tows of continuous filaments and impart antistatic properties to the fibers at both low and high humidity. The invention further provides fibers which are not moisture sensitive and which can be readily carded and spun into yarns over a broad range of atmospheric conditions.

These results are accomplished in the present invention by treating the fibers with aqueous dispersions containing (a) salts of polyoxyalkylene amines and mono and dialkyl esters of phosphoric acid or (b) salts of polyoxyalkylene amines and esters of polyoxyalkylene monoalkyl ethers with phosphoric acid.

It has previously been found that simple amine or alkanol amine salts of mono or dialkyl phosphoric acid will impart antistatic properties to fibers. Such disclosure is made in U.S. Pat. No. 2,676,122 issued to McCarthy Apr. 20, 1954, No. 2,676,924 to Summit et al. and U.S. Pat. No. 2,742,379 issued to Schofield Apr. 17, 1956. However, these materials alone do not yield satisfactory solutions or dispersions in water at concentrations desirable for application to fibers. Furthermore, the finish on the fibers becomes tacky when exposed to a slightly humid atmosphere. Such fibers will stick to cards and cause loading and will also stick to the rolls of the spinning machine and cause roll wraps. An antistatic finish must not only prevent a buildup of static on a fiber but it must give the fiber the proper degree of lubricity. The proper drag and adhesiveness and other qualities necessary for satisfactory processing into a finished yarn. The carding, drafting, and spinning operations are the most critical processing steps. The finish must also be easily applied in a uniform coverage of the fiber.

The finishes of the present invention meet these rigid requirements to a remarkable degree. The finishes are generally prepared as 1 to 6 percent aqueous solutions and form satisfactory low-viscosity low-surface tension solutions which will penetrate to cover the separate filaments of a heavy tow and uniformly coat the individual filaments. The finish can be applied to the tow or the cut staple fibers. The dried filaments will then not become tacky when exposed to humid atmospheres and usually contain about 0.1 to 1.5 percent by weight dry finish based on the fiber weight. The fibers can be carded and spun into highly uniform yarns without loading the cards and without troublesome roll wraps on the spinning machine.

The finishes of this invention are prepared by neutralizing polyoxyalkylene amines with mono or dialkyl phosphoric acid. Preferably the alkyl phosphoric acid is made from phosphoric acid and an ether of a polyoxyalkylene glycol and an alcohol.

The polyoxyalkylene amines are best prepared by reacting an alkyl amine or an alkanol amine with ethylene oxide. Many products of this type are commercially available. Propylene oxide can be used instead of ethylene oxide but the latter is more economical and is preferred.

Best results are obtained if the phosphate esters are made from alcohols which have first been reacted with an alkylene oxide, preferably ethylene oxide.

The following are some of the polyoxyalkylene amines useful in the present invention: lauryl amine (derived from coconut oil) reacted with 5 mols ethylene oxide; lauryl amine reacted with 15 mols ethylene oxide; decyl amine reacted with 10 mols ethylene oxide; tetradecyl amine reacted with 17 mols ethylene oxide; octyl amine reacted with 7 mols propylene oxide; octyl amine reacted with 8 mols ethylene oxide; 2-ethylhexyl amine reacted with 10 mols ethylene oxide; monoethanolamine reacted with 10 mols ethylene oxide.

The following alcohols and alcohol derivatives are suitable for the preparation of mono and dialkyl phosphate esters: lauryl alcohol; decyl alcohol; tetradecyl alcohol; hexadecyl alcohol; octadecenyl alcohol; octyl alcohol; lauryl alcohol reacted with 4 mols ethylene oxide; nonyl phenol reacted with 6 mols ethylene oxide; nonyl phenol reacted with 4 mols ethylene oxide; decyl alcohol reacted with 7 mols propylene oxide; tetradecyl alcohol reacted with 6 mols ethylene oxide; octadecenyl alcohol reacted with 4 mols ethylene oxide; decyl alcohol reacted with 3 mols ethylene oxide and 3 mols propylene oxide.

The commercially available amines and alcohols or alkyl phenols are not always pure compounds as regards chain length but purity in this sense is not necessary for purposes of this invention. However, the materials should be of good color and free of other chemical species. Octyl and decyl alcohols are most readily available commercially as a 50/50 mixture and such a mixture is satisfactory for purposes of this invention.

Phosphate esters usually consist of mixtures of the mono and diesters and these are satisfactory. Mixtures of alcohols or polyoxyalkylene glycol ethers of alcohols can be used to make the phosphoric acid esters.

Although the salt of the polyoxyalkylene amine and the phosphoric ester constitutes the essential ingredient of these finishes, it has been found that the viscosity control is improved if polyoxyalkylene ethers of certain phenols or polyoxyalkylene esters of certain organic acids or also included in the finishing solution. The following monoethers and esters of polyalkylene glycols are suitable for use in these finishes: lauric acid reacted with 9 mols ethylene oxide; decanoic acid reacted with 8 mols propylene oxide; nonyl phenol reacted with 4 mols ethylene oxide; octadecenoic acid reacted with 20 mols ethylene oxide; hexadecanoic acid reacted with a mixture of 10 mols ethylene oxide and 10 mols propylene oxide.

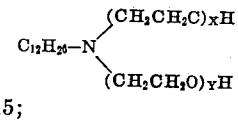
The following examples will give details of the application of this invention and clearly demonstrate its contribution to the art and science of producing textiles but will not limit the invention.

EXAMPLE I

A 1.5 denier (0.165 Tex) per filament tow is spun from a solution in dimethyl formamide of the following terpolymer:

Acrylonitrile	96.0 parts
Methylacrylate	3.6 parts
Sodium styrenesulfonate	0.4 parts

After stretching, washing, and crimping, the fibers are cut into 1.5-inch (3.8 cm.) length staple. For convenience, the finish is applied to the staple by dipping the staple into a 4 percent aqueous solution of a finish made by mixing together the following quantities of materials: 5 parts of a mixture of the mono and diesters of phosphoric acid with an ether made by reacting nonyl phenol with 6 mols ethylene oxide; 45 parts of an amine of the following formula



where $X+Y=15$;

50 parts polyethylene glycol monolaurate having a molecular weight of 400.

The excess solution is squeezed out of the fibers and they are dried in an oven at 130° C., leaving 0.5% finish on the dry weight of the fibers.

These fibers card well with no loading of the card and are spun into uniform yarns. No static charges develop.

When the finished and dried fibers are exposed to various humid atmospheres, they do not become tacky but remain smooth and slick.

In order to test the humidity effects on this finish, water is added in small quantities to the 100% finish, the viscosity increases only slightly as shown in the following table. The amounts of water shown correspond to the amounts of water that would be taken up under various atmospheric conditions.

Viscosities in Centipoises

Amounts of Water	At 50 r p m	At 500 r.p.m.
No water	140	155
3%	145	180
5%	145	185
10%	160	210
15%	165	225
20%	180	245

These relatively small viscosity changes with increasing mounts of water in the finish insure that the properties of the nished fiber will not vary widely with changes in humidity of ne air to which the fibers are exposed.

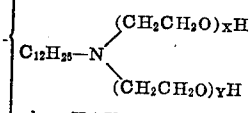
The surface tension of a 20 percent solution of this finish is found to be 34 dynes per cm.

Table 1 below shows finishing compositions for Examples 1, 2, and 3 along with some of the properties of the finish and of staple acrylic fibers (same as Ex. 1) having the finish thereon.

Table 2 below shows the processing properties of fibers finished in Examples 1, 2, and 3. Thus, it will be seen that these finishes give good protection from static development and also process satisfactorily through carding, drafting, and spinning operations.

Table 3 shows the composition of two finishes which were used at different concentrations on a high melting polyamide fiber of the type disclosed in U.S. Pat. No. 3,287,324 and Table 4 shows the processing properties of the fibers.

TABLE 1

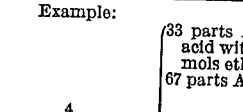
Example	Finish composition	Percent finish	Finish viscosity, c.p.	Coefficient of friction: High speed [1] low load	Coefficient of friction: Slow speed [2] high load	Static [3] generation	Log of resistence: 31% RH	Log of resistence: 65% RH	Log of resistence: 83% RH
1	5 parts A-1 a mixture of mono- and diesters of phosphoric acid with an ether made by reacting nonyl phenol with 6 mols of ethylene oxide. 45 parts A-2 an amine of the following formula:  where X+Y=15 50 parts A-3 a polyethylene glycol monolaurate having a molecular weight of 400.	0.5	200	0.37	0.26	+20	10.2	9.5	8.6
2	8 parts A-4 dioctyl phosphoric some monoester). 42 parts A-2 50 parts A-3	0.5	210	0.40	0.26	+5.0	10.2	9.5	8.6
3	12 parts A-5 dioeylester of phosphoric acid (contains some monoester). 38 parts A-2 50 parts A-3	0.5	220	0.38	0.24	+3.4	10.4	9.7	8.8

[1] Fiber on chrome.
[1] Fiber on fiber.
[3] Micro micro coulombs/cm. of yarn—for friction test see: Roder (Journal of the Textile Institute, pp. T-247 to T-251, June, 1953).

TABLE 2

	Carding efficiency, percent	Card loading	Static millivolts	Fly waste	Bulk	Web	Drafting stops	Spinning ends down	Roll wraps
Example:									
1	98	None	1-2	Med-high	High	Very good	1	5	0
2	97	do	0-2	do	do	do	1	2	1
3	97	do	0-2	do	do	do	0	0	0

TABLE 3

	Finish composition	Percent finish	Coefficient of friction: High speed [1] low load	Coefficient of friction: Slow speed [2] high load	Static [3] generation	Log Rp [4]
Example:						
4	33 parts A-6 mono- and diester of phosphoric acid with ether of lauryl alcohol reacted with 4 mols ethylene oxide. 67 parts A-7  where X+Y=15	0.4 0.8	0.84 0.91	0.25 0.28	+1.7 +0.1	9.4 8.5
5	5 parts A-1 (see Table 1 Example 1) 45 parts A-2 (from Table 1) 50 parts A-8 nonyl phenol reacted with 4 mols ethylene oxide.	0.4 0.8	0.77 0.89	0.35 0.34	+11.0 +0.4	+9.8 +9.5

[1] At 70 yards per minute (106 cm./sec.) with 10 gm. tension over smooth chrome finished surface.
[2] Yarn over yarn on spool at 0.001 cm./sec.
[3] Micro micro coulombs per cm. of yarn.
[4] Log R measured on a package of yarn.

TABLE 4

Example	Percent finish	Carding efficiency, percent	Card Loading	Static [1]	Fly waste	Bulk	Web appearance	Drafting stops	Sliver tenacity, milligrams: denier	Sliver tenacity, milligrams: texture	Percent Elongation	Spinning ends down	Roll wraps	Uster tensile, grams
4	0.17	97	Low	None	None	Low	Very good	1	1.9	0.21	8.2	1	1	514
	0.37	97	Med	do	do	Low	do	9	2.1	0.23	7.8	1	0	514
5	0.21	97	Low	20-40	do	Low	do	0	2.2	0.24	7.7	3	3	536
	0.71	97	Low	None	do	Low	do	0	3.2	0.35	7.0	3	3	487

[1] Millivolts on card web as measured with electrostatic voltmeter.

TABLE 5

Ex.	Finish composition	Log R values: On polyethyleneterephthalate polyester staple fibers at 0.2%; Relative humidity, percent: 34	65	83	On poly(hexamethyleneadipamide) polyamide staple fibers at 0.5%; Relative humidity, percent: 34	65	83
6	31 parts A-6 (see Table 3, Ex. 4); 69 parts A-9 polyethyleneglycol amine of 500 molecular weight.	10.8	9.4	8.4	10.0	8.9	7.9
7	61 parts A-1 (see Table 1, Ex. 1); 39 parts A-9 (see Ex. 6, above)	11.0	9.5	8.5	10.6	9.3	8.3
8	31 parts A-6 (see Table 3, Ex. 4); 69 parts A-10 polypropyleneglycol amine of 500 M.W.	11.6	10.5	9.6	11.2	10.1	9.2
9	27 parts A-4 (see Table 1, Ex. 2); 73 parts A-9 (see Ex. 6, above)	10.8	9.5	8.6	10.3	9.0	8.0
10	27 parts A-4 (see Table 1, Ex. 2); 73 parts A-10 (see Ex. 8, above)	11.6	10.4	9.7	11.3	10.2	9.4
11	35 parts A-11 dilauryl ester of phosphoric acid. 65 parts A-9 (see Ex. 6, above)	10.7	10.4	8.5	10.0	8.9	8.1
12	35 parts A-11 (see Ex. 11, above); 65 parts A-10 (see Ex. 8, above)	11.6	10.4	9.7	11.3	10.3	9.5
13	36 parts A-5 (see Ex. 3, above); 64 parts A-9 (see Ex. 6, above)	11.0	9.6	8.5	10.3	9.2	8.1
14	36 parts A-5 (see Ex. 3, above); 64 parts A-10 (see Ex. 8, above)	12.0	10.7	10.0	11.6	10.6	9.7
15	5 parts A-1 (see Table 1, Ex. 1); 45 parts A-2 (see Table 1, Ex. 1); 50 parts A-8 (see Table 3, Ex. 5)	----------			10.7	10.0	9.2

TABLE 6

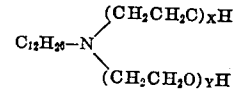
Ex.	Finish composition	Log R values on acrylic fibers at 0.5% relative humidity, percent: 31	65	83
16	17.4 parts A-11 (see Table 5, Ex. 11); 32.6 parts A-10 (see Table 5, Ex. 8); 50.0 parts A-3 (see Table 1, Ex. 1)	10.4	9.6	6.7
17	10 parts A-6 (see Table 3, Ex. 4); 20 parts A-7 (see Table 3, Ex. 4); 70 parts A-3 (see Table 1, Ex. 1, above)	10.4	9.5	8.6
18	5 parts A-1 (see Table 1, Ex. 1); 45 parts A-2 (see Table 1, Ex. 1); 50 parts A-3 (see Table 1, Ex. 1, above)	10.2	9.5	8.6
19	13 parts A-4 (see Table 1, Ex. 2); 37 parts A-10 (see Table 5, Ex. 8); 50 parts A-3 (see Table 1, Ex. 1, above)	10.5	9.8	9.0
20	17 parts A-5 (see Table 1, Ex. 3); 33 parts A-10 (see Table 5, Ex. 8); 50 parts A-3 (see Table 1, Ex. 1)	10.6	10.0	9.1
21	17 parts A-5 (seee Table 1, Ex. 3); 33 parts A-9 (see Table 5, Ex. 6); 50 parts A-3 (see Table 1, Ex. 1)	10.1	9.3	8.4
22	9 parts A-4 (see Table 1, Ex. 2); 41 parts A-7 (see Table 3, Ex. 4); 50 parts A-3 (see Table 1, Ex. 1)	10.3	9.5	8.5
23	12 parts A-11 (see Table 5, Ex. 11); 38 parts A-7 (see Table 3, Ex. 4); 50 parts A-3 (se Table 1, Ex. 1)	10.3	9.5	8.5
24	12 parts A-5 (see Table 1, Ex. 3); 38 parts A-7 (see Table 3, Ex. 4); 50 parts A-3 (see Table 1, Ex. 1)	10.4	9.7	8.8

Log_R is an expression for the static resistance of fibers. The measurements are made under controlled conditions of a specific relative humidity and a temperature of 70° F. Current flowing across the fibers from two electrodes is measured with a Beckman Model V Micro microammeter, and the surface resistance is then calculated from this and the known applied voltage. For convenience, these values are reported as logarithms of surface resistance.

What is claimed is:

1. A product of polyester, polyamide or polyacrylic staple material containing about 0.1 to 1.5 percent by weight of the staple of an antistatic agent consisting essentially of

1. about 38 parts of an amine of the formula



where $x+y=15$;

2. about 12 parts of the dioleyl ester of phosphoric acid; and

3. about 50 parts of polyethyleneglycol monolaurate having a molecular weight of about 400.

* * * * *

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(5/69)

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. U.S. 3,619,274 Dated November 9, 1971

Inventor(s) Thomas Jefferson Proffitt, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In column 2, line 55 (Example I), and in column 6, fifth line of Claim 1), the formula should read:

$$C_{12}H_{25}-N\begin{cases}(CH_2-CH_2-O)_xH\\(CH_2-CH_2-O)_yH\end{cases}$$

Signed and sealed this 23rd day of May 1972.

(Seal)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents