

# UNITED STATES PATENT OFFICE

2,676,122

## ANTISTATIC TREATMENT OF HYDROPHOBIC FIBER

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This invention relates to non-cellulosic, hydrophobic textile materials having improved physical characteristics. More particularly, this invention deals with fibers, filaments, fabrics or other forms of synthetic, non-cellulosic textile materials such as nylon, polyacrylonitrile, polyethylene terephthalate and their various modifications.

Fibers of the aforementioned type are well known for their poor electrical conductivity. As a result, they tend to accumulate electrostatic charges in working, as for instance in the textile mill, or in service, as for instance in a rug. Such charges may be annoying for instance by causing a nylon dress to cling to the body of the wearer, interfering with the intended graceful hang of the garment; but they are worse than annoying in the textile mill, where such static charges, formed through repeated friction of the fiber, filament or yarn, may prevent proper spinning, drawing, twisting, weaving or knitting.

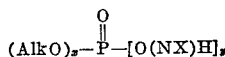
It is accordingly an object of this invention to provide textile materials of the aforementioned classes, which through treatment with an agent as defined below, shall be essentially free of noxious electrostatic qualities, or shall in any event be comparable in their working qualities to cotton, in so far as static charges are concerned.

Although the general idea of treating textile fiber with anti-static agents is old, the problem of selecting a proper agent is by no means a simple one. In the first place, the nature of the fiber to be treated must be taken into account. Thus, agents which have been indicated in the art as suitable for wool, viscose or cellulose acetate, do not as a rule produce good anti-static effects on hydrophobic, non-cellulosic fiber. Secondly, when an effective agent has been found it must answer still other qualifications; for instance, it must be compatible with lubricants, sizes and other agents commonly applied to fiber in the mill. It must allow proper running tensions of filament during drawing and twisting operations. It must be non-corrosive of the apparatus upon which the fiber will be worked, and it must be non-toxic and have no injurious dermatological effects upon the worker or upon the ultimate wearer.

Now, according to this invention excellent anti-static effects upon non-cellulosic, hydrophobic textile materials are obtained by using a special group of agents which may be defined broadly as mixtures of amine salts of long-chain alkyl phosphates, whereof the amine portion is an oxy-alkylene amine, such as mono-, di-, and

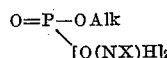
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triethanol amine, the ethanol derivatives of monomethyl and dimethyl amine, and morpholine. In other words, the group of agents found useful according to this invention are mixtures, composed of compounds defined by the general formula—

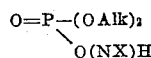


wherein  $x$  designates the numeral 1 or 2, while  $y$  is the difference between 3 and  $x$ , Alk is a normal, alkyl radical having from 8 to 16 carbon atoms, and NX represents an oxyalkylene amine selected from the group consisting of the three ethanolamines, the three ethanol-methylamines (i. e. monoethanol-mono-methylamine, ethanol-dimethylamine and diethanol-methylamine), and morpholine.

I find that I obtain best results with mixtures of amine-salts of various alkyl-phosphates. Thus, a mixture of 90 mole percent of—



and 10 mole percent of



gives very much superior results to an agent consisting of the pure diamino-monoester. The superiority of the agent increases as the proportion of diester in the mixture increases, and for a 50:50 mixture it reaches a maximum appreciably superior to that obtainable from either of its pure components. The anti-static effects are nevertheless still very high when the agent consists of pure monoamino-diester. Altogether then, it may be summarized as a general rule that the agent according to this invention should comprise a reaction product of phosphorus pentoxide, a straight-chained saturated primary, monohydric alcohol of more than 6 carbon atoms and an oxyalkylene amine as above defined, with the proviso that the reaction product shall comprise at least substantial quantities of the monoamino diester component.

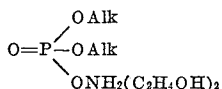
In addition, they have the quality of being readily soluble in alcohol and self-dispersible in water, so that they may be applied to the fiber from either medium.

Their electrostatic effect is very high and rates from good to excellent in standard tests recently developed for measuring anti-static effects.

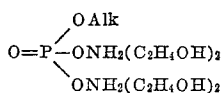
A particularly good effect is obtained when NX in the above general formula is a diethanolamine, and the best results in this group are

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obtained when the agent is an essentially equimolecular mixture of two esters of the formula



and



which is obtained for instance by reacting one mole of phosphorus pentoxide with about 3 moles of the selected alcohol and then reacting this intermediate product with 3 moles or more of diethanolamine.

The quantity of agent required per unit weight of fiber is not high. A loading of agent as low as 0.02 gm. per 100 gm. of fiber will produce a remarkable improvement in electrical conductivity. Loadings as high as 2% by weight of the fiber may be used. More commonly, however, loadings of 0.04 to 0.4% will be found both satisfactory and economical.

Without limiting my invention the following examples are given to illustrate my preferred mode of operation. Parts mentioned are by weight.

#### PART A.—PREPARATION OF THE AGENTS

##### Example 1

To a stirred mixture of 1 mole of n-octanol-1, 1 mole of n-decanol-1, and 1 molecular equivalent of "Lorol" (a commercial mixture of primary alcohols, predominantly C<sub>12</sub> and C<sub>14</sub>) was added over a period of 1.5 hours 1 mole of phosphorus pentoxide, keeping the reaction temperature below 40° C. The mixture was then stirred at 50°-55° C. for 1.5 hours and then further stirred at 60°-65° C. until complete solution was effected. Three moles of diethanolamine were then added to the hot reaction mixture at such a rate as not to permit the reaction temperature to exceed 80° C., and stirring was continued until the exothermic reaction subsided. The product was a yellow, oily liquid.

##### Example 2

Three moles of n-octanol-1 were substituted for the alcohol mixture used in Example 1. The product was a clear liquid.

##### Example 3

A mixture of 1.5 moles of n-hexanol-1 and 1.5 moles of cetyl alcohol was substituted for the alcohol mixture used in Example 1. The product was a soft grease.

##### Example 4

The procedure was as in Example 1, but three moles of "Ocenol" (octadecanol-1) were used, yielding a dark brown thick oil.

##### Example 5

The procedure was as in Example 1, but instead of diethanolamine, 3 moles of monoethanolamine were used. This yielded a dark brown grease.

##### Example 6

The procedure was as in Example 1, but instead of diethanolamine, 3 moles of triethanolamine were used. The product was a red-brown heavy oil.

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##### Example 7

The procedure was as in Example 1, except using 3 moles of morpholine. This gave a clear, medium-viscosity, red brown oil.

##### Example 8

The procedure was as in Example 1, except using 3 moles of dimethylethanolamine. A reddish oil was obtained.

##### Example 9

The procedure was as in Example 1, except using 3 moles of methyldiethanolamine. The product was a yellow oil.

##### Example 10

The procedure was as in Example 2, except using 2.75 moles of octanol-1 to 1 mole of P<sub>2</sub>O<sub>5</sub>. The product was a yellow brown grease.

##### Example 11

The procedure was as in Example 2, except using 3.75 moles of octanol-1 to 1 mole of P<sub>2</sub>O<sub>5</sub>. The product was yellow orange oil.

##### Example 12

In a manner similar to Examples 10 and 11, by varying the proportion of alcohol to P<sub>2</sub>O<sub>5</sub> in the first part of the process, the following three compositions of matter were prepared and isolated:

- (a) bis-diethanolamine salt of monolauryl phosphate;
- (b) the diethanolamine salt of dilauryl phosphate;
- (c) and equimolecular mixture of (a) and (b).

These were used for the tests described in Example 19 hereinbelow.

#### PART B.—APPLICATION

The evaluation of electrostatic properties in the examples hereinbelow was carried out essentially as follows:

A small piece of hydrophobic fabric (approximately 4" x 5") is weighed under conditions of controlled humidity and immersed for 30 sec. in approximately 330 cc. of a 95% ethanol solution of the anti-static agent containing 1 g. of the agent. The fabric is removed, air-dried, and weighed again to provide a basis for calculating the pick-up of anti-static agent. For comparative tests, a loading of 0.06% agent on nylon taffeta was adopted as standard.

A strip 3 cm. wide is then cut off, and its electrical resistance at a controlled relative humidity of 25% is measured on a special apparatus which comprises two electrodes separated by a space of 1.25 cm. and having a potential difference of 90 volts. The fabric is held in place between the electrodes so as to provide a conducting area 1.25 cm. long and 3 cm. wide. The reading gives the resistance of this standard area in ohms. For practical purposes the results are rated as follows:

Resistance	Anti-static rating
Less than 50×10 <sup>8</sup> ohms.....	Excellent.
50-500×10 <sup>8</sup> ohms.....	Very good.
500-2,500×10 <sup>8</sup> ohms.....	Good.
2,500-10,000×10 <sup>8</sup> ohms.....	Fair.
10,000-100,000×10 <sup>8</sup> ohms.....	Poor.
More than 100,000×10 <sup>8</sup> ohms.....	Nil.

(The rating of the untreated control in the non-cellulosic, hydrophobic fibers herein discussed is usually nil.)

## Example 13

Each agent whose preparation is described in Examples 1 to 11 was applied separately to nylon, polyacrylonitrile and polyethylene terephthalate woven fabrics. This was done by padding for approximately 30 seconds in 250 parts by weight of 95% ethanol containing 1 part by weight of the anti-static agent. After wringing the fabrics to wet pick-ups of 0.1-0.3 (ratio of liquid to dry fabric by weight), the fabrics were air-dried. Active ingredient loadings of 0.04-0.12% (based on dry weight of fabric) were then obtained. Electrical resistance of the treated fabrics, as measured by the above-described standard method, were as follows:

Product	Anti-static Rating
Ex. 1.....	Excellent.
Ex. 2.....	Very good.
Ex. 3.....	Do.
Ex. 4.....	Good.
Ex. 5.....	Very good.
Ex. 6.....	Do.
Ex. 7.....	Do.
Ex. 8.....	Do.
Ex. 9.....	Excellent.
Ex. 10.....	Very good.
Ex. 11.....	Do.

## Example 14

The materials and procedure were the same as in Example 13, except that water was substituted for the ethanol as vehicle for the anti-static agent. The pad baths had the appearance of colloidal solutions. Since the water pick-up of fabrics is 10-15% higher than alcohol pick-up, the concentration of agents in the aqueous pad baths was reduced by a corresponding amount. The electrical resistance in each case, was found to be practically identical.

## Example 15

Nylon, polyacrylonitrile and polyethylene terephthalate fabrics were treated by the method of Example 13, using the product of Example 1 in ethanol solutions of sufficiently increased concentrations to produce loadings of 2.0% by weight. The treated fabrics had anti-static ratings of "excellent." The coatings were of a lubricative nature, but they were not objectionably oily.

## Example 16

200 parts of the product of Example 1 were dispersed in 250 parts of water containing 3.5 parts of a sodium alkylsulfate prepared from higher alcohols averaging C<sub>10</sub>. The resulting emulsion was mixed very vigorously and 200 parts of a high boiling white mineral oil (boiling range, 300-350° C.) were stirred in. The resulting paste had an active ingredient content of 61%. A spinning finish bath was prepared by dispersing 100 g. of this paste in 500 g. of water. It was applied to nylon filament immediately after extrusion of the melt, by passing the filament tangentially over a glass wheel revolving in the bath. In this manner loadings of the anti-static agent amounting to from 0.05 to 0.4% by weight of the filament were obtained. The anti-static rating of the treated fibers was excellent.

In this same manner nylon fiber has been treated with numerous other anti-static agents falling within the above general formula. In every

case an excellent anti-static effect was imparted to the fiber.

## Example 17

To 100 parts of an emulsion of medium viscosity mineral oil (40 sec. white oil) in water containing 11.2% oil, 3 parts of the alkyl phosphate described in Example 1 were added. This mixture was run through a Disper-mil, and a homogeneous emulsion was obtained. It contained 11.2% oil solids, 3% anti-static agent and 85.8% water.

In substantially the same manner as described in Example 13, a loading of 0.5% total finish was applied to nylon fiber, giving approximately 0.11% of the anti-static agent on the fiber. The fiber had an anti-static rating of "excellent."

When the same procedure was applied to polyacrylonitrile fiber and to polyethylene terephthalate fiber, similar, high anti-static effects were obtained.

## Example 18.—Compatibility with coning oils

Five parts of the composition described in Example 1 were dissolved in 100 parts of butyl palmitate (a conventional coning oil), using approximately 5 parts of ocnol as solubilizing agent. The resulting solution was applied to nylon fiber by passing the fiber over a roll in contact with the oil. The treated fiber was found to have an anti-static rating of good to excellent.

## Example 19.—Superiority of mixed agents

(a) The bis-diethanolamine salt of monolauryl phosphate was applied to nylon from an alcoholic bath, in the manner described in Example 13, to produce various loadings ranging from 0.04 to 0.12% by weight. In all cases, the anti-static qualities of the fabric were found to rate "poor" to "fair," on the above standard table.

(b) When the diethanolamine salt of dilauryl phosphate was tested in the same manner and in the same range of loadings, the treated fabric tested "good."

(c) In the same manner an agent made from three moles of diethanolamine and a 1:1 molar mixture of mono- and dilauryl phosphate was tested and found to have an anti-static rating of "very good."

It will be understood that the details of the above examples and procedures may be varied widely, within the skill of those engaged in this art.

Thus, in the synthesis of the agent, the reaction between phosphorus pentoxide and the selected alcohol (or mixture of alcohols) and the subsequent reaction between the intermediate esters thus obtained with the selected oxy-alkylene amine, are both exothermic and require cooling; but the ultimate temperature maintained during each step of the reaction may be anywhere between 20° and 100° C.

The products can be applied to hydrophobic fibers in several ways. Filaments may be treated immediately after extrusion of the hydrophobic melt or solution. A tow of many threads of spun filament may be treated at some stage prior to the crimper, as in the manufacture of staple fiber. The agents may also be applied in the coning or winding oil, in a sizing bath or in a padding bath for fabric or skeins.

For the purpose of comparison, many agents of a chemical structure falling outside the limits

of the generic formula hereinabove have been tested by me by the same standard process as hereinabove. The following tables show the anti-static ratings thus obtained. All tables refer to esters obtained as above by reacting a mixed alkyl phosphate (1 mole P<sub>2</sub>O<sub>5</sub>:3 moles of the respective alcohol) with an oxy-alkylene amine as named in each case.

TABLE I.—USING DIETHANOLAMINE THROUGHOUT

Esterifying group	Anti-static rating
Mixed n-C <sub>3</sub> to n-C <sub>18</sub> alkyl.....	excellent.
n-octyl.....	very good.
n-C <sub>6</sub> + n-C <sub>10</sub> alkyl (1:1).....	Do.
n-octadecyl.....	good.
n-propyl.....	nil.
n-butyl.....	Do.
sec-amyl.....	Do.
2-ethyl butyl.....	poor.
methyl-isobutyl-methyl (from methyl-isobutyl carbinol).....	Do.
di-isopropyl methyl (from di-isopropyl carbinol).....	nil.
mixed heptyl and higher alkyl (secondary, branched).....	poor.
2-ethyl hexyl.....	fair.
trimethyl hexyl.....	poor.
cyclohexyl.....	Do.
oxy-bisethylene (from diethylene glycol).....	fair.
mixed n-C <sub>3</sub> and higher alkyl + oxy-bisethylene.....	Do.
the radical of blown castor oil.....	poor.
the radical of raw castor oil.....	Do.

TABLE II.—USING THROUGHOUT THE MIXED ALKYL ESTER DEFINED IN EXAMPLE I

Amine or base	Anti-static rating
diethanolamine.....	excellent.
monoethanolamine.....	very good.
triethanolamine.....	Do.
morpholine.....	Do.
dimethylethanolamine.....	Do.
methyldiethanolamine.....	excellent.
diethylenetriamine.....	nil.
beta-aminoethyl-ethanolamine.....	poor.
glycine.....	Do.
ammonia.....	nil.
pyridine.....	Do.
sodium hydroxide.....	Do.

It is clear from the above tables that only when the alkyl radical is longer than C<sub>6</sub> and only when the amine is an oxy-alkylene amine as above defined does the mixture of alkyl amine phosphates give anti-static ratings better than fair.

In addition, the preferred agents of this invention were tested for other qualities essential for their use in treating textiles, such as ease of dispersion, stability of the aqueous emulsion, rate of pick-up by the fiber, stability to heat and to storage, and compatibility with the other agents with which they were applied. In all cases my preferred agents as defined by the above general formula were found to rate good to very good. All these qualities make my novel agents additionally valuable for use in spinning finishes, staple finishes, coning and winding oils and in sizing baths. Furthermore, they can be sprayed onto waste fibers which accumulate in textile processing mills, so that these scraps can be recovered by passing them through the picking and carding operations without interference by electrostatic charges.

As for the chemical nature of the fiber to be treated, this invention is applicable in general to non-cellulosic, hydrophobic textile fibers. Hereinabove we have discussed nylon, polyethylene terephthalate, polyacrylonitrile and their various modifications. As instances of the latter may be mentioned polymers of acrylonitrile

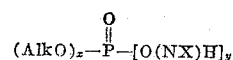
which have been modified by copolymerization with substantial amounts of other vinyl compounds such as vinyl pyridine, vinyl chloride, styrene or vinyl acetate; polyacrylonitrile which is mixed with other materials such as plasticizers, modifiers, etc.; linear polyesters of ethylene glycol and terephthalic acid which have been modified by the addition of up to 10% of other glycols and/or dibasic acids; and polyethylene terephthalate which is mixed with other materials such as plasticizers, modifiers, etc. These fibers are all well known in the literature, and many of them are common commercial products. See for instance, Carothers, U. S. P. 2,071,250; 2,071,253 and 2,130,948; Whinfield et al., U. S. P. 2,465,319; Jacobson, U. S. P. 2,436,926; Latham, U. S. P. 2,404,714 and Arnold, U. S. P. 2,491,471.

It will be understood that although this specification is concerned primarily with textile fibers, my novel agents may be applied also to the above indicated chemical materials in non-textile form, for instance sheets or shaped masses.

These agents are effective on any hydrophobic substrate which tends to accumulate an electrical charge. Such substrates may also include polyethylene, polystyrene, polyvinyl chloride, polyvinylidene chloride, copolymers of these chlorides with acrylonitrile, polytetrafluoroethylene, polychlorotrifluoroethylene, copolymers of the latter two, polyvinyl fluoride, etc., in either fiber or massive form.

I claim:

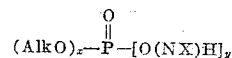
1. A process of improving the electrostatic qualities of non-cellulosic, hydrophobic textile fiber which comprises impregnating the same with a mixture of agents of the general formula



wherein Alk represents a straight-chained, saturated primary aliphatic hydrocarbon radical of 8 to 16 C-atoms, NX represents an oxyalkylene amine selected from the group consisting of the ethanolamines, the N-methyl-ethanolamines and morpholine;  $x$  is an integer not greater than 2, while  $y$  is the difference between 3 and  $x$ .

2. A process of improving the electrostatic qualities of non-cellulosic, hydrophobic textile fiber which comprises impregnating the same with an agent comprising a diethanolamine salt of mixed mono- and di-alkyl phosphates, the alkyl radical whereof is a straight-chained, saturated, aliphatic, primary, hydrocarbon radical of 8 to 16 C-atoms.

3. Non-cellulosic, hydrophobic textile fiber having incorporated therein from 0.02 to 2.0% by weight of an antistatic agent of the general formula



wherein Alk represents a straight-chained, saturated, aliphatic, primary, hydrocarbon radical of 8 to 16 C-atoms, NX represents an oxyalkylene amine selected from the group consisting of the ethanolamines, the N-methyl-ethanolamines and morpholine;  $x$  is an integer not greater than 2, while  $y$  is the difference between 3 and  $x$ .

4. Non-cellulosic, hydrophobic textile fiber having incorporated therein from 0.02 to 2.0% by weight of an antistatic agent, the latter comprising a mixture of the diethanolamine salts of mono- and di-alkyl phosphates, the alkyl radical

whereof is a straight-chained, saturated, aliphatic, primary hydrocarbon radical of 8 to 16 C-atoms.

5 5. Non-cellulosic, hydrophobic textile fiber having incorporated therein from 0.02 to 2.0% by weight of a composition of matter being a substantially equimolecular mixture of monoalkyl-bis(diethanolamine)-phosphate and dialkyl-mono(diethanolamine)-phosphate, wherein the alkyl radical is a straight-chained, saturated, 10

aliphatic, primary hydrocarbon radical of from 8 to 16 C-atoms.

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