最新国外合成纤维油剂·助剂技术专利大全

最新国外合成纤维油剂、助剂技术专利大全

（上　册）

抚顺市科技情报研究所

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抚顺市石油化工科技情报研究所

《最新国外合成纤维油剂、助剂技术专利大全》目录

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Saiki et al.

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[54] **ANTISTATIC AGENTS FOR SYNTHETIC FIBERS**

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[58] **Field of Search** 252/8.8, 8.6; 57/901

[56] **References Cited**

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[57] **ABSTRACT**

Antistatic agents for synthetic fibers comprising 5–50 weight percent of a specific type of quaternary ammonium alkyl phosphate containing 1 weight percent or less of by-product alkali metal halides and 50–95 weight percent of alkali metal salt of saturated alkyl phosphate have improved antistatic characteristics both in high and low humidity conditions, reduce the amount of deposits that fall off, yellowing by a heat treatment and generation of rust, and allow good coiling forms to be obtained.

4 Claims, No Drawings

ANTISTATIC AGENTS FOR SYNTHETIC FIBERS

This invention relates to antistatic agents for synthetic fibers.

In general, static electricity presents problems to synthetic fibers not only in the manufacturing process of filament yarn and staple fiber, spinning process, weaving process and finishing process but also regarding products made from them. Static electricity impedes operations and lowers the quality of products by dishevelling and wrapping and producing fluff. It thus gives shocks to people, causes the clothes to stick and attracts dust particles. It is therefore necessary to use an antistatic agent with synthetic fibers but such an antistatic agent must be able to exhibit its effectiveness not only under a condition of high humidity but also when humidity is low.

During the production of synthetic fibers, finishing oil which fall off and deposit themselves on the machines during each process present serious problems. During a spinning process, for example, the fibers may be caused to wrap around a draft rubber roller. If they fall off onto a guide or a trumpet, these machine parts must be cleaned more frequently. If they fall off onto a heater during a spinning-drawing process, tar will be generated. If they fall off onto a guide during a warping process, it will generate fluff and cause yarn breakage. As the processing speed is increased, the problems caused by the deposit become even more serious and this necessarily implies that antistatic agents to be applied to synthetic fibers must have the property of not falling off at a significant rate. The present invention relates to antistatic agents for synthetic fibers having this required characteristic.

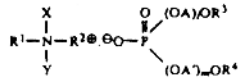
There are many types of surface active agents (cationic, anionic, non-ionic and amphoteric) serving as antistatic agents for synthetic fibers. Alkyl phosphates exhibit favorable antistatic properties under conditions of high and medium humidity, do not fall off very much, do not turn yellow by a heat treatment and do not rust much, but are not as effective as desired as an antistatic agent in low humidity situations.

Quaternary ammonium salts such as trimethyl lauryl ammonium chloride, triethyl polyoxyethylene (3 mols) stearyl ammonium methosulfate, and tributyloctyl ammonium nitrate have also been used as antistatic agents. These quaternary ammonium salts are advantageous in that they exhibit favorable antistatic properties not only at high humidity but also at low humidity but they fall off, turn yellow by a heat treatment and generate rusts.

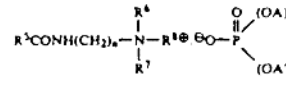
These problems associated with quaternary ammonium salts, however, are thought to be caused by the counter anions of quaternary ammonium cations. In fact, if the counter anion is Cl^-, rusting becomes a serious problem and if it is NO_3^- or $CH_3SO_4^-$, yellowing becomes serious. Earlier, quaternary ammonium salts with phosphate anion introduced as counter anion came to be considered (Japanese Patent Tokko 45-573 and Tokkai 54-70223). These quaternary ammonium lower alkyl phosphates exhibit favorable antistatic properties both at high humidity and at low humidity and have the advantages of not turning yellow much by a heat treatment and not producing much rust, but have the problem of falling off significantly.

It is therefore an object of the present invention to eliminate the aforementioned problems by providing antistatic agents for synthetic fibers which are capable of exhibiting favorable antistatic properties under both high and low humidity conditions and do not fall off, turn yellow by a heat treatment or rust much.

An antistatic agent for synthetic fibers according to this invention comprises 5–50wt % of quaternary ammonium alkyl phosphates shown by the formula (I) or (II) below and not containing more than 1wt% of by-product alkali metal halides and 50–95wt% of alkali metal salts of saturated alkyl phosphate with 50% or more of alkyl groups with 18 or more carbon atoms:



(I)

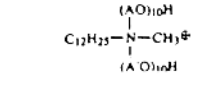


(II)

where R^1 and R^3 are alkyl group or alkenyl group with 8–18 carbon atoms, R^2, R^6, R^7 and R^8 are alkyl group with 1–3 carbon atoms, R^4 is hydrogen or alkyl or alkenyl group with 8–18 carbon atoms, R^5 is alkyl or alkenyl group with 7–17 carbon atoms, X is alkyl group with 1–3 carbon atoms or a group shown by $-(AO)_qH$, Y is alkyl group with 1–3 carbon atoms or a group shown by $-(A'O)_rH$, AO and A'O being the same respectively as OA and OA' in the formulas (I) and (II), q and r are integers in the range of 2–40 such that $q+r=4$–42, OA and OA' are a single oxyethylene or oxypropylene group or a block or random connected mixture thereof, l and m are each zero or an integer in the range of 1–20 such that $l+m=0$–20, and n is 2 or 3.

In the formulas (I) and (II), if the number of carbon atoms in R^1 and R^3 is less than 8 or that in R^5 is less than 7, the amount of deposit increases. If the content of by-product alkali metal halides exceeds 1wt% with respect to the quaternary ammonium alkyl phosphate, there is increased yellowing by a heat treatment and rusting. For this reason and in particular for preventing rust, particular preferable content of alkali metal halides which is particularly preferable is 0.3wt% or less with respect to quaternary ammonium alkyl phosphate.

Examples of quaternary ammonium alkyl phosphate of the present invention shown by the formula (I) or (II) include combinations of the following quaternary ammonium cations and phosphate anions. The quaternary ammonium cations may be trimethyloctyl ammonium cation, triethylstearyl ammonium cation,



where AO and A'O are the same as in (I), triethyl octanoic amidopropyl ammonium cation, etc. The phosphate anion may be polyoxyethylene (3 mols) lauryl phosphate anion, polyoxyethylene (10 mols) stearyl phosphate anion, octyl phosphate anion, etc.

In the following, methods of producing quaternary ammonium alkyl phosphates of this invention will be explained. Because of their characteristic chemical structures, the quaternary ammonium alkyl phosphates of the present invention cannot be produced advanta-

geously from a practical point of view by any of the conventional methods. There has been known a method, for example, of preventing alkali metal halides from being produced as by-products by direct reaction between tertiary amine and lower alkyl triester of phosphoric acid (Japanese patent Tokko 45-573 and Tokkai 54-70223), but since triesters of phosphoric acid with a long-chain alkyl group have low reactivity with tertiary amines, they are not practical for the production of quaternary ammonium long-chain alkyl phosphates.

According to another conventional method, an alkali metal salt of mono- and/or di-long-chain alkyl phosphate is reacted with mono-long-chain alkyl tri-short-chain alkyl ammonium halide by a salt exchange in water or an alcohol solvent such as methanol, isopropanol, etc. Quaternary ammonium alkyl phosphates are the produced by filtering inorganic by-product compounds such as alkali metal halides. Although this conventional method is popular for the production and refining of so-called complex salts which are combinations of anion and cation active agents, it is not appropriate for keeping the content of inorganic by-products to 1wt% or less because both the quaternary ammonium halide and the alkali metal salt of alkyl phosphate to be used contain long-chain alkyl groups and it is stoichiometrically difficult to carry out the salt exchange reaction for increasing their concentrations to relatively high levels in the range of 10–50wt% in water or alcohol-type solvent which are required for industrial reasons. Accordingly, there will remain unused quaternary ammonium halides and alkali metal salts of alkyl phosphate and this makes it practically impossible to reduce the content of alkali metal halides to 1wt% or less with respect to quaternary ammonium alkyl phosphates.

Quaternary ammonium alkyl phosphates according to this invention can be produced by the method described below. First, tertiary amine shown by the following formula (1) or (2) is quaternalized by alkyl halide (with alkyl group given by R^2 or R^8 of (I) or (II)). Next, lower alcoholate of alkyl metal is used in the presence or absence of lower alcohol as solvent to exchange the halogen anions of the anion part with lower alcoxy anions, and after the alkali metal halides generated at this time as by-products are separated, mono- or di-alkyl phosphate shown by the following formula (3) is used to exchange the alcoxy anions:

(1)

(2)

(3)

where R^1, R^3, R^4, R^5, R^6, R^7, X, Y, l, m and n are as defined above.

Examples of alkali metal alcoholate which may be used here include sodium methylate, sodium ethylate and potassium isopropoxide, but sodium methylate is industrially advantageous. Favorable results are obtained in view of the salt exchange reaction and the separation process thereafter, if lower alcohol such as methanol, ethanol and isopropanol is used as solvent. Thus, quarternary ammonium alkyl phosphates of the present invention are mixtures of mono alkyl phosphate and dialkyl phosphate of quarternary ammonium.

Quaternary ammonium alkyl phosphates of the present invention can be used singly as an antistatic component of a finishing oil for synthetic fibers but there are situations in which they prove to be even more effective if used as an appropriate mixture with a conventional antistatic agent. For example, a mixture with an appropriate amount of quaternary ammonium alkyl phosphate added to an antistatic agent of alkyl phosphate type not only provides to synthetic fibers an antistatic property to such a degree that was totally unexpected from a single alkyl phosphate system but also prevents the wrapping and falling off and a good coiling form can be obtained.

Representative examples of alkyl phosphate type antistatic agent of which the effectiveness can be significantly improved by the addition of an appropriate amount of quaternary ammonium phosphate of the present invention include alkali metal salts of saturated alkyl phosphate having as principal component alkyl group with 18 or more carbon atoms. In such a mixed system, the content of the quaternary ammonium alkyl phosphate of the present invention should be 5–50wt%. Although the optimum ratio varies, depending on the kinds of quaternary ammonium alkyl phosphate and alkali metal salt of alkyl phosphate, a particularly preferable range is 5–20wt% of quaternary ammonium phosphate (that is, 95–80wt% of alkali metal salt of alkyl phosphate). The antistatic agents of this invention can be applied singly to synthetic fibers such as polyesters, polyacrylonitriles and polyamides or to their mixtures with natural and chemical fibers. The rate of application to such synthetic fibers (inclusive of mixed fibers) is generally 0.01–2wt% and preferably 0.01–0.5wt%. They may be applied to filaments, a tow or staple fibers by a kiss-roll method, by dipping or by spraying either during or after a spinning process. They may also be applied to fiber products.

In what follows, the present invention and its effects will be explained further in detail by way of examples and comparisons and it should be understood that these examples are not intended to limit the scope of this invention.

TEST NO. 1

Synthesis of quaternary ammonium alkyl phosphate of this invention (Example A-1):

One mol of phosphoric anhydride was added to three mols of octyl alcohol over a period of one hour at 60°-70° C. while stirring. They were allowed to react with each other at 70° C. for three hours and a mixture of mono and dioctyl phosphate was obtained. Separately, 0.5 mol of octyl dimethylamine and 200 ml of methanol were set inside an autoclave and after the interior gas was replaced by nitrogen, 0.5 molar equivalent of methyl chloride was introduced for a reaction at 60°-70° C. for three hours to obtain octyltrimethyl ammonium chloride. To this was gradually added 96 g of 28% sodium methylate-menthanol solution (0.5 molar equivalent as sodium methylate) for salt exchange and the by-product sodium chloride was filtered away to obtain a methanol solution of octyltrimethyl ammonium

methoxide. To this methanol solution was added 0.5 mol of the aforementioned mixture of mono and dioctyl phosphate and after methanol was distilled away, it was diluted with water to obtain 50wt% aqueous solution of octyltrimethyl ammonium octyl phosphate (A-1).

Other quaternary ammonium alkyl phosphates (A-2 through A-11 and B-1 through B-16 except B-12; only those starting with the letter A are quaternary ammonium alkyl phosphates of this invention) were synthesized as follows.

SYNTHESIS OF A-2 THROUGH A-11

They were obtained by methods similar to the method for A-1.

SYNTHESIS OF B-1 THROUGH B-8

They were obtained by methods similar to the method for A-1.

B-9 THROUGH B-12

Conventionally available products were used.

SYNTHESIS OF B-13

This was done by heating to dissolve 347.5 g (1 mol) of stearyl trimethyl ammonium chloride and 334.7 g (1 mol) of sodium sesqui stearyl phosphate in 2000ml of a mixed solvent of isopropyl alcohol/water = 95/5 (volume ratio). The solution was heated and stirred for one hour at 60° C. and the deposited sodium chloride was filtered away by heating at 45°–50° C. Isopropyl alcohol was distilled from the filtered solution thus obtained while heating under a reduced pressure and trimethyl stearyl ammonium stearyl phosphate with 80% of solid component was obtained.

SYNTHESIS OF B-14

This was done by dissolving with heat 347.5 g (1 mol) of stearyl trimethyl ammonium chloride and 668 g (1 molar equivalent) of 50% aqueous sodium sesqui stearyl phosphate in 2000 ml of isopropyl alcohol and 1000 ml of water and isopropyl alcohol was distilled away under azeotropy while the mixture was heated and stirred. Next, 1000 ml of isopropyl alcohol was added to dilute the solution and sodium chloride which deposited at 35°–40° C. was filtered away. Isopropyl alcohol was distilled away by heating under a reduced pressure from the filtered solution which had been obtained and trimethyl stearyl ammonium stearyl phosphate with 80% of solid component was obtained.

SYNTHESIS OF B-15

This was obtained by a method similar to that for B-13.

SYNTHESIS OF B-16

This was obtained by a method similar to that for B-14.

Each of the examples shown below (except B-12) is described as follows: (1) cation part (2) anion part (mixture of mono and di as in the case of aforementioned A-1, except B-9 through B-12), and (3) content of alkali metal halide (NaCl or KCl) with respect to effective components (weight percent, measured by the Volhard method except for B-9 through B-12). POE, POP and EO respectively stand for polyoxyethylene, polyoxypropylene and oxyethylene.

A-1: (1) trimethyl octyl ammonium, (2) octyl phosphate, (3) 0.18

A-2: (1) trimethyl octyl ammonium, (2) stearyl phosphate, (3) 0.14

A-3: (1) trimethylstearyl ammonium, (2) octyl phosphate, (3) 0.14

A-4: (1) trimethylstearyl ammonium, (2) stearyl phosphate, (3) 0.10

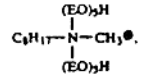
A-5: (1) triethyl octanoic amido propyl ammonium, (2) POE (4 mols) octyl phosphate, (3) 0.20

A-6: (1) triethyl octanoic amido propyl ammonium, (2) POE (15 mols) stearyl phosphate, (3) 0.24

A-7: (1) triethyl stearoic amido propyl ammonium, (2) POE (2 mols)/POP (1 mol) octyl phosphate, (3) 0.23

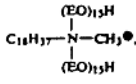
A-8: (1) triethyl stearoic amido propyl ammonium, (2) POE (5 mols)/POP (1 mol) stearyl phosphate, (3) 0.24

A-9: (1)



(2) octyl phosphate, (3) 0.63

A-10: (1)



(2) stearyl phosphate, (3) 0.27

A-11: (1) trimethyloctyl ammonium, (2) octyl phosphate, (3) 0.80

B-1: (1) trimethylhexyl ammonium, (2) octyl phosphate, (3) 0.25

B-2: (1) trimethylhexyl ammonium, (2) stearyl phosphate, (3) 0.20

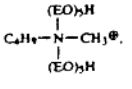
B-3: (1) trimethyloctyl ammonium, (2) butyl phosphate, (3) 0.34

B-4: (1) triethyl butanoic amido propyl ammonium, (2) octyl phosphate, (3) 0.75

B-5: (1) triethylbutanoic amido propyl ammonium, (2) stearyl phosphate, (3) 0.63

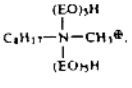
B-6: (1) monomethyl dioctylbutanoic amido propyl ammonium, (2) butyl phosphate, (3) 0.01

B-7: (1)



(2) octyl phosphate, (3) 0.83

B-8: (1)

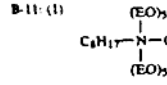


(2) butyl phosphate, (3) 0.72

B-9: (1) trimethyloctyl ammonium, (2) chloride

B-10: (1) triethyloctylamidpropyl ammonium, (2) methosulfate

B-11: (1)



(2) nitrate

B-12: (1) potassium lauryl phosphate

B-13: (1) trimethylstearyl ammonium, (2) stearyl phosphate, (3) 2.10

B-14: (1) trimethylstearyl ammonium, (2) stearyl phosphate, (3) 1.43

B-15: (1) trimethyloctyl ammonium, (2) octyl phosphate, (3) 2.47

B-16: (1) trimethyloctyl ammonium, (2) octyl phosphate, (3) 1.71

The following measurements and evaluations were made regarding A-1 through A-11 and B-1 through B-16.

MEASUREMENT OF ELECTRICAL RESISTANCE AND EVALUATION OF YELLOWING

Staple fiber samples were prepared by applying 0.1% (effective weight percent) of each example by a spray method to polyester staple fibers (1.4-denier, 38 mm) and dried for one hour at 60° C. These samples were left for 24 hours under the conditions of 25° C. and 40%RH or 25° C. and 65%RH, and their electrical resistance was measured. They were also subjected to a heat treatment at 150° C. for two hours and the degrees of their yellowing were observed and evaluated visually.

MEASUREMENT OF ELECTROSTATIC CHARGE GENERATED BY FRICTION

Pieces of refined woven acrylic cloth were immersed in 0.2% (effective weight percent) water solution of each example and then dried for one hour at 60° C. They were left for 24 hours under the conditions of 25° C. and 40%RH and their static charges were measured by a rotary static tester.

EVALUATION OF DEPOSIT THAT FALL OFF

Staple fiber samples were prepared by applying 0.12% (effective weight percent) of each example by a spray method to polyester staple fibers (1.4-denier, 38 mm) and were left for 24 hours under the conditions of 30° C. and 70%RH. These samples were used and 10 kg of slivers manufactured by a carding engine was passed through a drawing frame. The deposits that fall off and become adhered to the trumpet to which the sliver is taken up were visually observed. Grades A through E were assigned in the increasing order of the amount of deposits, grade A being given if this amount is very small.

EVALUATION OF RUSTING

After washed knitting needles were immersed in 2% (effective weight percent) water solutions of individual examples, they were left for 24 hours under the conditions of 20° C. and 100%RH and the appearance of rust on each needle was visually observed and evaluated.

The results of the above are shown in Tables 1 and 2.

TABLE 1

A-No	Resistance (Ω) 25° C., 40% RH	Resistance (Ω) 25° C., 65% RH	Static Charge (V)	Deposit	Yellowing	Rust
1	1.2×10^7	8.8×10^5	100	A	None	None
2	4.3	16	200	A	None	None
3	5.7	33	170	A	None	None
4	8.5	53	450	A	None	None
5	3.2	13	180	A	None	None
6	6.5	45	250	A	None	None
7	6.3	43	210	A	None	None
8	8.8	74	470	A	None	None
9	1.3	9.0	100	A	None	Slight
10	3.3	21	120	A	None	None
11	1.5	8.5	100	A	None	Slight

TABLE 2

B-No	Resistance (Ω) 25° C., 40% RH	Resistance (Ω) 25° C., 65% RH	Static Charge (V)	Deposit	Yellowing	Rust
1	1.0×10^7	11×10^5	110	E	Slight	None
2	4.2	10	170	D	None	None
3	3.2	9.5	100	E	Slight	None
4	3.5	21	210	E	None	None
5	4.7	3.5	350	D	None	None
6	15	170	700	D	None	None
7	1.3	12	100	E	None	None
8	1.1	8.8	100	E	None	None
9	3.5	22	210	D	Present	Great
10	3.1	36	480	E	Present	Great
11	7.7	44	400	E	Present	Great
12	600	890	1400	A	None	None
13	8.3	61	430	B	Present	Great
14	8.4	59	400	A	Slight	Great
15	1.1	17	90	E	Slight	Great
16	4.0	15	360	D	Slight	Great

TEST NO. 2

Emulsions were prepared from individual finishing oil (sample of present invention 1-12 and comparison samples 1-9) having compositions (weight percent) shown in Tables 3 and 4 and fiber samples were produced by applying 0.15wt% of each by the spray method individually to polyester staple fibers (1.4-denier, 38 mm) and leaving for 24 hours under the temperature and humidity conditions shown in Tables 5 and 6. The following measurements were made and evaluated. The results of the test are shown in Tables 5 and 6.

MEASUREMENT OF ELECTRIC RESISTANCE

Measurements were taken as in Test No. 1.

MEASUREMENT OF ROLLER WRAPPING

Roving yarns produced from the fiber samples by using a roving frame were spun out of a spinning frame and the number of the fibers wrapped around the rubber roller (manufactured by Yamanouchi Rubber Company, hardness 82 degrees) was counted.

EVALUATION OF DEPOSITS

Testing and evaluation were done as in Test No. 1.

EVALUATION OF COILING FORM

Samples were processed to drawing frame and the forms of the produced silver coils were evaluated and graded similarly into five levels from A (very good) to E (not good).

TABLE 3

	(Samples of present invention)						
No.	A-1	A-4	A-5	A-10	P-1	P-2	P-3
1	5				95		
2	10				90		
3		10			90		
4			10		90		
5	15					85	
6				15			85
7	20				80		
8		20				80	
9	30				70		
10		30				70	
11			40				60
12	45				55		

TABLE 4

	(Comparison samples)									
No.	A-1	A-4	B-15	B-16	B-13	B-3	P-1	P-2	P-4	P-5
1			5				95			
2			10			90				
3		15					85			
4		30				70				
5				30			70			
6	10							90		
7		20							80	
8	30								70	
9						10	90			

In Tables 3 and 4, A-1 through A-10 and B-1 through B-16 are the same as previously defined. P-1, P-2 and P-3 are all potassium salts of saturated alkyl phosphate with octadecyl/hexadecyl=90/10, 85/15 and 65/35, respectively. P-4 and P-5 are respectively potassium hexadecyl phosphate and potassium dodecyl phosphate.

TABLE 5

	(Samples of present invention)				
	Resistance (Ω)		Wrapping (times)	Deposit	Coiling Form
No.	25° C., 40% RH	25° C., 65% RH	30° C., 70% RH	30 ° C., 70% RH	30° C., 70% RH
1	9.2×10^7	12.5×10^5	0	A	A
2	6.3	10.0	0	B	B
3	7.4	11.2	0	A	A
4	4.5	8.2	1	B	B
5	6.0	9.5	0	B	B
6	3.0	7.0	7	B	C
7	2.8	6.5	2	B	B
8	7.2	10.5	0	A	A
9	2.5	5.4	7	B	B
10	5.3	9.0	6	B	B
11	1.4	3.2	10	B	C
12	1.8	3.6	8	B	C

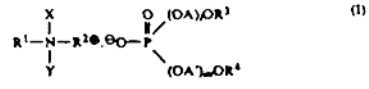
TABLE 6

	(Comparison samples)				
	Resistance (Ω)				
No.	25° C., 40% RH	25° C., 65% RH	Wrapping (times)	Deposit	Coiling Form
1	9.0×10^7	11.8×10^5	7	C	E
2	6.0	9.6	10	C	E
3	6.2	9.0	12	D	E
4	2.0	5.2	15	D	E
5	4.9	8.8	20	E	E
6	8.3	10.3	18	B	E
7	2.1	5.1	15	C	E
8	1.0	2.8	17	C	E
9	6.2	8.9	[illegible]	D	D

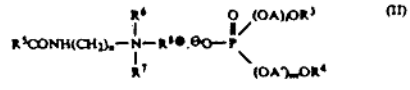
Comparisons between Tables 1 and 2 and between Tables 5 and 6 clearly demonstrate that the finishing oil of the present invention described hereinabove exhibit superior antistatic characteristics both in high humidity and low humidity conditions, reduce the amount of deposits that fall off, yellowing by a heat treatment and generation of rust, and allow good coiling forms to be obtained.

What is claimed is:

1. An antistatic agent for synthetic fibers comprising 5–50 weight percent of quaternary ammonium alkyl phosphate which is shown by the formula (I) or (II) below and contain 1 weight percent or less of by-product alkali metal halides and 50–95 weight percent of alkali metal salt of saturated alkyl phosphate with 50% or more of alkyl groups with 18 or more carbon atoms;



(I)



(II)

where R^1 and R^3 are alkyl group or alkenyl group with 8–18 carbon atoms, R^2, R^6, R^7 and R^8 are each alkyl group with 1–3 carbon atoms, R^4 is hydrogen or alkyl group or alkenyl group with 8–18 carbon atoms, R^5 is alkyl group or alkenyl group with 7–17 carbon atoms, X is alkyl group with 1–3 carbon atoms or a group shown by $-(AO)_lH$, Y is alkyl group with 1–3 carbon atoms or a group shown by $-(A'O)_mH$, AO and A'O are respectively the same as OA and OA' in the formulas (I) and (II), q and r are integers in the range of 2–40 such that q+r=4–42, OA and OA' are single oxyethylene or oxypropylene group or block or random connected mixture thereof, l and m are 0 or integers in the range of 1–20 such that l+m=0–20, and n is 2 or 3.

2. The antistatic agent of claim 1 comprising 5–20 weight percent of said quaternary ammonium alkyl phosphate and 80–95 weight percent of said alkali metal salt of saturated alkyl phosphate.

3. The antistatic agent of claim 1 wherein said quaternary ammonium alkyl phosphate is obtained by the steps of

quaternalizing tertiary amine shown by the formula (1) or (2) by using alkyl halide with 1–3 carbon atoms,

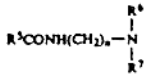
subsequently using alkali metal alcoholate to exchange halogen anions in anion section for alcoxy anions,

separating alkali metal halide generated as a by-product, and

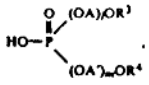
subsequently exchanging said alcoxy anions by using mono- or di-alkyl phosphate shown by the formula (3):

(3)

-continued



(2)



(3)

where R^1, R^3, R^4, R^5, R^6, R^7, X, Y, l, m and n are the same as in the formulas (I) and (II).

4. The antistatic agent of claim 2 wherein said quaternary ammonium phosphate is obtained by the steps of

quaternalizing tertiary amine shown by the formula (1) or (2) by using alkyl halide with 1-3 carbon atoms,

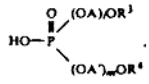
subsequently using alkali metal alcoholate to exchange halogen anions in anion section for alcoxy anions,

separating alkali metal halide generated as a by-product, and

subsequently exchanging said alcoxy anions by using mono- or di-alkyl phosphate shown by the formula (3):

(1)

(2)



(3)

where R^1, R^3, R^4, R^5, R^6, R^7, X, Y, l, m and n are the same as in the formulas (I) and (II).

* * * * *

United States Patent [19]

Yamamoto et al.

[11] **Patent Number: 4,505,956**

[45] **Date of Patent: Mar. 19, 1985**

[54] **LUBRICANT FOR TREATING SYNTHETIC FIBERS**

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[73] Assignee: **Takemotoyushi Co. Ltd.,** Aichiken, Japan

[21] Appl. No.: **456,018**

[22] PCT Filed: **Apr. 30, 1982**

[86] PCT No.: **PCT/JP82/00148**

§ 371 Date: **Dec. 27, 1982**

§ 102(e) Date: **Dec. 27, 1982**

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PCT Pub. Date: **Nov. 11, 1982**

[30] **Foreign Application Priority Data**

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[51] Int. Cl.³ D06M 13/20; D06M 13/16; D06M 13/40; C09K 3/16

[52] U.S. Cl. 427/393.1; 252/8.8

[58] Field of Search 252/8.8; 427/393.1

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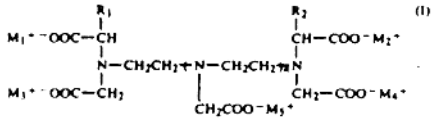
Primary Examiner—Maria Parrish Tungol

Attorney, Agent, or Firm—Fred Philpitt

[57] **ABSTRACT**

This invention is directed to a lubricant for treating synthetic fibers characterized by adding a polyethylenepolyaminepolyacetic acid derivative of the following formula (I) to a composition comprising so far known lubricating agent and surfactant, and imparts lubricating property and antistatic property to synthetic fibers in the production and processing steps thereof:



(I)

wherein R_1 and R_2 is hydrogen or an alkyl or alkenyl group of 1-22 carbon atoms; n is an integer of 0-4; and M_1^+-M_5^+ are respectively selected from the group consisting of hydrogen ion, alkali metal ion, and ammonium ion expressed e.g. by the following formula (II):

(II)

wherein R_3, R_4 and R_5 are respectively selected from the group consisting of hydrogen, alkyl, alkenyl, hydroxyalkyl, polyethoxyalkyl, polypropyleneoxyalkyl and polyethylenepolyaminoethyl.

4 Claims, No Drawings

LUBRICANT FOR TREATING SYNTHETIC FIBERS

FIELD OF THE ART

This invention relates to a novel lubricant for treating synthetic fibers which is suitable for applying a lubricant containing a specified compound to synthetic fibers to thereby impart a high extent of lubricating property and antistatic property to fiber filaments in the production step and the processing step of synthetic fibers and diminish various obstacles in the steps.

ART OF THE BACKGROUND

Generally in the case of thermoplastic synthetic fibers such as polyester, nylon, polypropylene, etc., a lubricant for treating fibers is attached to unstretched yarns obtained by melt-spinning, followed by stretching to 3 to 4 times the original length and heat-set for fixing the properties. The resulting stretched yarns are further passed through advanced processing steps such as bulky processing, twisting, warping, sizing, knitting, weaving, etc. to give fiber products, and in such production and processing steps, yarns are industrially treated very often at considerably high speed for improving their productivity; thus various obstacles accompanying the treatment such as attrition of guides, travellers, knitting needles, etc. contacting with filaments, various electric obstacles such as fiber-breakage due to approach of filaments at the time of warping, contact thereof with the second heater and twining round nip rolls in a false twist processing machine, etc. have become a more and more serious problem. Thus a fiber-treating lubricant capable of diminishing such obstacles has been earnestly required.

As an antistatic agent component for fiber-treating lubricants used in the production and processing steps of synthetic fibers, various kinds of anionic surfactants, cationic surfactants, amphoteric surfactants, etc. have so far been used in admixture, but those which satisfy all of problems of antistatic property, lubricating property to metals, the so-called lubricating property and collecting property such as high speed unwinding from pirn, cheese, etc., resistance to attrition of metals, and the like properties, have not yet been developed. Further, when lubricants using such ionic surfactants are made up into an aqueous emulsion to be applied to fibers, the resulting foam is too large, resulting in adhesion unevenness of lubricants; hence development of an antistatic agent having little foaming property has been particularly awaited.

Further, surfactants as the above-mentioned component being currently most often used for the antistatic purpose are anionic surfactants, but those having properties which fully satisfy the above-mentioned purpose under a severe condition of an atmosphere of extremely low humidity (RH: 30% or lower), have not yet been found. For example, as anionic surfactants used so far, there are alkali metal salts or alkanolamine salts of long-chain alkyl phosphates, which, however, have drawbacks of being liable to wear frictional bodies as described above and lowering antistatic property at the time of high temperature heat treatment or at the time of low humidity. Further, surfactants of alkylsulfate salt or alkylsulfonate salt type exhibit superior antistatic property under an atmosphere of high humidity or medium humidity, but they are not yet fully satisfactory under an atmosphere of extremely low humidity (RH: 30% or lower), and if the amount thereof added is increased in order to supplement the insufficiency of the property, their lubricating property becomes notably inferior, and further, when they are dissolved in water, their emulsion causes a notable foaming due to reduction in the surface tension.

Furthermore, aliphatic carboxylic type anionic surfactants represented by alkali metal salts of oleic acid or ricinoleic acid exhibit desirable properties in the aspect of antistatic property as compared with the above-mentioned other anionic surfactants, but their antistatic property under an extremely low humidity and their properties in the case where the amount thereof added is increased, have similar drawbacks to those of the above-mentioned alkylsulfate salt and alkylsulfonate salt type surfactants.

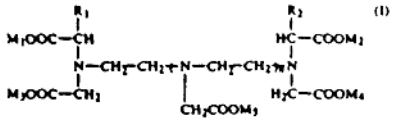
Further, in order to improve sizing property, generally the proportion of anionic surfactants in the lubricant may be increased, but this case also exhibits similar drawbacks to the above-mentioned. Further, in the case where polymers having a number of carboxyl groups in the molecule such as copolymers of maleic anhydride with a water-soluble vinyl monomer or alkali metal salts or ammonium salts of polyacrylic acid, etc. are used as a fiber-treating agent, they exhibit an excellent effectiveness of improving collecting property, but, on the other hand, friction of fibers to metals at high speed is very great, and also such carboxylic acid salts of polymers have almost no antistatic effectiveness.

DISCLOSURE OF THE INVENTION

In view of the above-mentioned various points, the present inventors have made strenuous studies for obtaining a fiber-treating lubricant which can notably inhibit the static build-up phenomenon of synthetic fibers even under a condition of an atmosphere of extremely low humidity to thereby notably alleviate static troubles at various steps, and at the same time can prevent the attrition of guides, pins, etc. in contact with fiber filaments running at a high speed, and also is superior in the collecting property and lubricating property. As a result the present inventors have found that (poly)ethylenepolyaminepolyacetic acid derivatives exhibit a superior antistatic property even under the above-mentioned extremely low humidity and are notably effective also in the attrition to metals and collecting property, and have attained the present invention.

The object of the present invention is to provide a fiber-treating lubricant which effectively inhibits the static electricity generated by friction of fiber filaments to guides, rolls, heaters, etc. during the production and processing steps of synthetic fibers, even under an extremely low humidity (RH: 30% or lower); prevents the attrition of frictional bodies such as guides, pins, etc. in contact with fiber filaments to be treated at a high speed, and also imparts a high extent of lubricating property and collecting property to fiber filaments.

Namely the present invention is directed to a lubricant (or an oiling agent) for treating synthetic fibers (hereinafter referred to as treating lubricant of the present invention), characterized in that it contains a (poly)ethylenepolyaminepolyacetic acid derivative (hereinafter referred to as compound of the present invention) expressed by the following general formula (I), in a composition comprising so far known mineral oil, ester or polyglycol lubricating agents and nonionic surfactants or ionic surfactants, etc.



wherein the symbols have the following meanings:

R_1, R_2: hydrogen atom or alkyl or alkenyl group of 1 to 22 carbon atoms;

M_1, M_2: a single member or a mixture of the following members (1) to (6):

(1) hydrogen atom or alkali metal cation,

(2) mono-, di- or tri(hydroxyalkyl)amine (the alkyl group having 2 to 4 carbon atoms),

(3) mono-, di- or trialkyl (and/or alkenyl)amine (the alkyl group and alkenyl group having 1 to 22 carbon atoms),

(4) secondary or tertiary amine having the hydroxyalkyl group and the alkyl group (and/or alkenyl group) in the amines of said (2) and (3) bonded to the nitrogen atom,

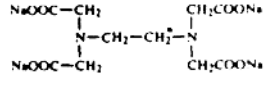
(5) addition product of ethylene oxide (and/or propylene oxide) to a compound having an active hydrogen atom among the compounds of said (2), (3) and (4) (the polymerization degree of ethylene oxide and/or propylene oxide being 1 to 20), and

(6) polyethylenepolyamine (the number of ethylene group being 1 to 5); and

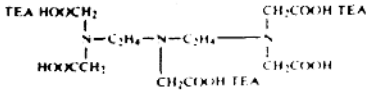
n: integer of 0 to 4.

Concrete examples of the compounds of the present invention are as follows, but the present invention is not limited only thereto:

(A) Sodium salt of ethylenediaminotetraacetic acid

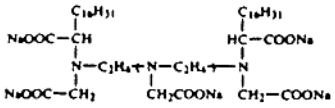


(B) Triethanolamine salt of diethylenetriamine-pentaacetic acid

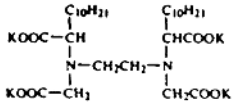


wherein TEA: triethanolamine

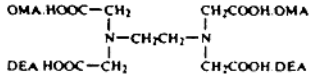
(C) Sodium salt of N,N'-bis(1-carboxyundecyl)ethylenediaminediacetic acid



(D) Potassium salt of N,N'-bis(1-carboxydecyl)ethylenediaminediacetic acid



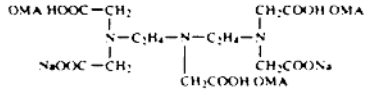
(E) Mixed salt of ethylenediaminetetraacetic acid and diethanolamine



wherein OMA: oleylmethylamine

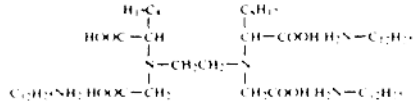
DEA: diethanolamine $HN(C_2H_4OH)_2$

(F) Oleylmethylamine-sodium mixed salt of diethylenetriaminepentaacetic acid

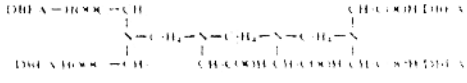


wherein OMA: oleylmethylamine

(G) Laurylamine salt of N,N'-bis(1-carboxynonyl)ethylenediaminediacetic acid



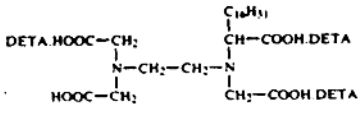
(H) Dibutylethanolamine salt of triethylenetetraminehexaacetic acid



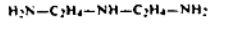
(I) Sodium salt of N,N'-bis(1-carboxyundecyl)tetraethylenepentaminoacetic acid

wherein DBEA

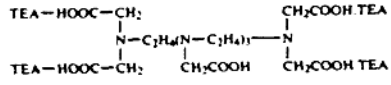
(I) Diethylenetriamine salt of N-(1-carboxyheptadecenyl)ethylenediaminetriacetic acid



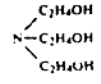
wherein DETA: diethylenetriamine:



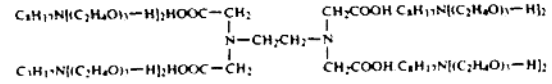
(J) Triethanolamine salt of tetraethylenepentaminehepta acetic acid



wherein TEA:



(K) POE (6) octylaminoether salt of ethylenediaminetetraacetic acid



The present invention provides a fiber-treating lubricant having a (poly)ethylenepolyaminepolyacetic acid derivative blended therein as an antistatic agent component, and the blending proportion of the compound has no particular limitation, but essentially the proportion may be in a range in which the effectiveness of the present invention can be exhibited; its content in the treating lubricant is usually in the range of 0.1 to 50% by weight, preferably in the range of 0.5 to 20% by weight.

The lubricating agent used together with the compound of the present invention in the treating lubricant of the present invention can be selected from among purified mineral oils, synthetic fatty acid esters and polyoxyalkylene glycols. As the purified mineral oils, those having a Redwood kinetic viscosity at 30° C. of 40 to 500 seconds may be used, and as the synthetic fatty acid esters, esters of aliphatic monobasic acids with aliphatic monohydric alcohols, esters of polyols such as ethylene glycol, diethylene glycol, neopentyl glycol, trimethylolpropane, glycerol, pentaerythritol, etc. with aliphatic monobasic acids or esters of aliphatic dibasic acids with aliphatic monohydric alcohols may be used.

Further concrete examples of the above-mentioned synthetic fatty acid esters are as follows:

butyl stearate, n-octyl palmitate, 2-ethylhexyl palmitate, oleyl laurate, isohexadecyl laurate, isostearyl laurate, dioctyl sebacate, diisotridecyl adipate, ethylene glycol dioleate, trimethylolpropane trioctanoate, pentaerythritol tetraoctanoate. Further, as examples of polyoxyalkylene glycols, those obtained by subjecting propylene oxide and ethylene oxide to random or block addition polymerization to butanol, octanol, lauryl alcohol, stearyl alcohol or the like, those obtained by subjecting propylene oxide and ethylene oxide to random or block addition polymerization to propylene glycol, trimethylolpropane, glycerol, pentaerythritol, sorbitol or the like, etc., having various molecular weights, may be used.

Next, examples of nonionic surfactants used together with the compounds of the present invention in the lubricant of the present invention are polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl esters, partial alkyl esters of polyols, etc.

Further, emulsification modifier, wetting agent, mildewproofing agent, rustproofing agent, etc. may be added to the above-mentioned various blend compositions, and the total amount of these additives is preferred to be 5% by weight or less based on the total blend composition.

The treating lubricant of the present invention, when applied to synthetic fibers as spinning lubricant or finishing lubricant, exhibits its effectiveness, and the lubricant, when used, is preferably attached to synthetic fibers in the form of an aqueous emulsion of 5 to 30% or in the form of a liquid obtained by diluting it with an organic solvent such as hydrocarbons, etc.

The treating lubricant of the present invention exhibits its its effectiveness in the production and processing steps of thermoplastic synthetic fibers such as polyamides, polyesters, polypropylene, etc., and it is particularly effective as spinning lubricant for polyester or polyamide filaments.

The present invention will be further described by way of Examples.

EXAMPLES 1-5 AND COMPARATIVE EXAMPLES a-g

Using the compounds (G) and (H) of the present invention as an antistatic agent, treating agents 1-5 of the present invention having compositions indicated in Table 1 were prepared. On the other hand, as Comparative examples, using 4 kinds of ionic surfactants indicated in Table 1, which have so far been used as an antistatic agent, fiber-treating lubricants a-g indicated in the Table were prepared.

With these lubricants, (1) antistatic property in an atmosphere of medium humidity, (2) antistatic property in an atmosphere of extremely low humidity, (3) fiber to metal kinetic frictional coefficient, and (4) fiber to fiber kinetic frictional coefficient were tested, followed by evaluation.

Blending of lubricants and results of tests carried out with the resulting blends are shown in Table 1.

As seen from Table 1, conventional antistatic agents are not yet sufficient in the antistatic property and also certain drawbacks are observed in other properties, whereas the treating lubricants of the present invention using the compounds of the present invention are notably superior in the antistatic property not only in an atmosphere of medium humidity, but also in an atmosphere of extremely low humidity, and in addition, other properties are not adversely affected.

was subjected to measurement of electricity generated on the filaments according to the same method and conditions as in the above (1) except that the atmosphere during the measurement was 25% RH.

Evaluation standard is the same as in the above (1).

(3) Fiber to metal kinetic frictional coefficiency:

A sample yarn prepared in the same manner as in the case of the above-mentioned measurement of antistatic property, was measured according to the following

TABLE 1

Lubricant No.	Example 1	2	3	4	5	Comparative example a	b	c	d	e	f	g
Lubricant component												
PO/EO (50/50) monooctyl ether (M.W. 2,000, random addition)	35	35	35	35	35	35	35	35	35	35	35	35
PO/EO (50/50) glyceryl ether (M.W. 4,000, random addition)	40	40	40	40	40	40	40	40	40	40	40	40
POE (3) lauryl ether	8	8	10	125	10	5	10	10	10	10	10	10
POE (20) hardened castor oil ether	12	12	12	12	10	10	10	10	10	10	145	145
*Compound of present invention (G)	5				1							
Compound of present invention (H)		5	3	0.5	1							
Potassium oleate salt						10	5					
POE (5) laurylphosphatetriethanolamine salt								5				
Sodium laurylsulfonate salt					3				5		0.5	
Oleylimidozoline quaternary salt										5		0.5
Test results												
Amount of lubricant attached (based on wt. % of fiber)	0.48	0.48	0.46	0.48	0.48	0.48	0.48	0.47	0.46	0.48	0.52	0.49
(1) Antistatic property in medium humidity atmosphere (20° C., 65% RH)		○	○	○	○	○	○	△	○	○	△	×
(2) Antistatic property in extremely low humidity atmosphere (20° C., 25% RH)	○	○	○	○	○	△	×	×	△	×	×	×
(3) Fiber to metal kinetic frictional coefficient	○	○	○	○	○	×	△	△	△	△		
(4) Fiber to fiber kinetic frictional coefficient	○	○	○	○	○	×	△	△	△	△		

Numerals in the Table represent the amounts of respective components blended (% by weight)
*Compounds (G) and (H) of the present invention are the same as those described above

Tests of the properties (1), (2), (3) and (4) in Table 1 were carried out according to the following methods and the results were evaluated with symbols shown on the right side of the respective testing methods:

(1) Antistatic property in an atmosphere of a medium humidity:

A lubricant to be tested was attached to multifilament of polyester stretched yarn SD (semidull) 75 deniers/36 filaments, in an amount of 0.5±0.1%, and subjected to moisture conditioning in an atmosphere of 65% RH at 20° C. to obtain a sample yarn.

This sample yarn was supplied into a measurement room having an atmosphere of 65% RH at 20° C., under an initial tension of 20 g and at a yarn speed of 300 m/min.; thereafter contacted with a stainless heater of 90 cm long kept at 200° C.; thereafter further contacted in frictional manner with a chrome-satinized frictional body at a contact angle of 90°; and subjected to measurement of electricity generated on the filaments by means of a collector type charge gauge (manufactured by Kasuga Denki) provided just therebehind.

Evaluation standard:

○	static build-up voltage	0–50 volt
△		51–100 volt
×		101–500 volt
		higher than 501 volt

(2) Antistatic property in an atmosphere of an extremely low humidity:

A sample yarn oiled under the same conditions as those of the above (1) and at the same time was subjected to moisture conditioning under 25% RH at 20° C. to obtain a sample yarn to be tested. This sample yarn was subjected to measurement of electricity generated on the filaments by means of a collector type charge gauge (manufactured by Kasuga Denki) provided just therebehind in the same manner as in the above (1) except that the atmosphere during the measurement was 25% RH.

Evaluation standard is the same as in the above (1).

(3) Fiber to metal kinetic frictional coefficiency:

A sample yarn prepared in the same manner as in the case of the above-mentioned measurement of antistatic property, was measured according to the following method by means of μ meter (manufactured by Eiko Sokki):

A yarn supplied under an initial tension (T_1) of 20 g and at a speed of 100 m/min. was contacted in frictional manner with a chrome-satinized pin at a contact angle of 90° in an atmosphere of 25% RH at 20° C., and a tension (T_2) just after passage through the frictional body was recorded, followed by calculating the kinetic frictional coefficient according to the following equation:

$$\mu = \frac{1}{\theta} \ln \frac{T_2}{T_1}$$

θ: contact angle
ln: natural logarithm

The higher the μ value in this method is, the more the tension on the surface of contact of the yarn is liable to rise and vary.

Evaluation standard:

○		μ: 0–0.25
△		μ: 0.26–0.30
×		μ: 0.31–

(4) Fiber to fiber kinetic frictional coefficient:

A sample yarn prepared in the same manner as in the case of the above-mentioned measurement of antistatic property, was measured under the following conditions by means of a radar type fiber friction meter (manufactured by Aoi Seiki).