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LUBRICANT COMPOSITION FOR SYNTHETIC FIBERS

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No Drawing. Continuation-in-part of application Ser. No. 526,390, Feb. 10, 1966. This application Jan. 14, 1969, Ser. No. 791,152

Claims priority, application Japan, Feb. 13, 1965, 40/7,904

Int. Cl. D06m *13/44*

U.S. Cl. 252—8.8 2 Claims

ABSTRACT OF THE DISCLOSURE

An antistatic lubricant composition is comprised of from 10 to 50% by weight of an imidazoline in which a carboxyethoxyethyl group is substituted at the 1-position, the composition also including from 40 to 80% by weight of a lubricating compound selected from the group consisting of a mineral oil or a fatty acid ester.

This application is a continuation-in-part of our copending application Ser. No. 526,390, filed Feb. 10, 1966, now abandoned.

The present invention relates to an oil in water type lubricant composition having the property of forming a stable emulsion and which is useful for preventing electrification of synthetic fibers.

1-ethylol-2-alkyl-2-imidazolines obtained by the reaction of fatty acids and hydroxyethyldiamine have been already marketed under the trademarks Amine 220 (U.C.C.), Nopcogen (Nopco Chemical Co.), etc. However, they are used as cationic surface active agents and since they will be combined with anionic ions when they are used for the purpose of this invention, they are unsuitable as emulsifying agents for lubricant compositions. Further, amphoteric surface active agents obtained by the reaction of the above-mentioned compounds and monochloroacetic acid have been marketed under the trademark Miranol (Miranol Chemical Co.), etc., but they also are unsuitable for the purpose of this invention because, although they have an antistatic electricity property to some extent, they have very low compatibility with lubricant components.

Therefore, an object of this invention is to provide a lubricant composition for synthetic fibers, which composition forms a stable emulsion and, when applied to synthetic fibers, gives an excellent antistatic electricity property to the fibers.

The lubricant composition of the present invention having an excellent antistatic electricity property comprises (1) as an essential component a surface active agent obtained by carboxyethylating a 1-ethylol-2-alkyl-2-imidazoline with methyl acrylate, (2) as a lubricating component a mineral oil or fatty ester, and (3) as an emulsifying agent a nonionic surface active agent or an anionic surface active agent.

The application of a lubricating oil to synthetic fibers has hitherto been carried out by (1) a method wherein spun filaments are passed through an aqueous emulsion

of a lubricating oil, or (2) by a so-called straight method wherein filaments are passed through a lubricating oil containing no water, or the filaments contact, while travelling, the surface of a roller on which a lubricating oil is carried. However, since in the latter method the amount of the lubricating oil applied to the filaments is large, which rather lowers the lubricating property of the filaments, the former method is usually adopted. That is, the former method is preferable because suitable amounts of a lubricating oil and water are applied to the filaments due to the use of an aqueous emulsion of the lubricating oil and because the amount of the lubricating oil applied to the filaments can be easily controlled.

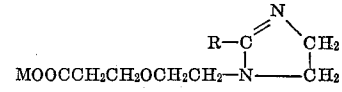
However, in this case, the uniformity of the emulsion particles of the lubricating oil and the stability of the emulsion are very important. For example, if filaments are treated with a lubricating oil using an unstable emulsion, tension stains are formed when the filaments are contacted with a metallic roller or guide after the application of the lubricating oil, breakage of the filaments occurs, and the quality of the fibers is greatly lowered.

Therefore, it has been desired to provide a lubricating composition for synthetic fibers which has an excellent antistatic electricity property and which is in the form of a stable and uniform emulsion.

As the lubricating component for such a composition there is usually used a mineral oil or a fatty acid ester. As an emulsifying agent for the mineral oil, there have hitherto been used polyoxyethylenated fatty acids, higher alcohols, or aliphatic alkylamines or amides, but they are not always suitable as an emulsifying agent for the fatty acid ester.

The lubricant composition, according to the present invention, has the property of providing a very stable emulsion as well as an antistatic electricity property.

The above imidazoline compound used as an essential component in the antistatic lubricant composition of this invention is an amphoteric surfactant and is a substituted imidazoline of the formula:



wherein R is an alkyl or alkenyl group containing from 8 to 22 carbon atoms, preferably from 11 to 17 carbon atoms such as undecyl, pentadecyl, heptadecyl, heptadecenyl and coconut alkyl and M is an alkali metal such as sodium and potassium.

The above fatty acid ester used as a lubricating component in the composition of this invention is an ester of a saturated or unsaturated fatty acid containing from 6 to 22 carbon atoms with a saturated or unsaturated alcohol containing from 6 to 22 carbon atoms, a glycerine monoester or diester of a saturated or unsaturated fatty acid containing from 6 to 22 carbon atoms, an ester of a dibasic acid containing from 6 to 10 carbon atoms with a saturated or unsaturated alcohol containing from 6 to 13 carbon atoms. The preferred compounds of these esters will be shown in the following examples of the invention.

In the lubricant composition of this invention, the ratio of each component may be varied in a wide range but,

in general, a lubricant composition having the following component ratio range is satisfactory and effective.

Component:	Weight percent
Lubricating component	40–80
Amphoteric surfactant	10–50
Emulsifying agent	0–40

The composition may contain a coupling agent if necessary.

The emulsifying agent in the lubricating composition of this invention is one or a mixture of various anionic or nonionic surface active agents and the coupling agent in the composition is an emulsifying aid, such as, a higher alcohol and a higher aliphatic acid.

The lubricating composition of this invention may usually be used in the form of an oil in water type emulsion and the concentration of the lubricating composition in the emulsion is usually 5–30% by weight. The proportion of the lubricating composition applied to filaments or fibers is usually 0.2–1.0% by weight, preferably about 0.2–0.5% by weight.

The present invention will now be explained with reference to the accompanying examples which will show the preferred embodiments of the invention as well as several comparative test results made by the use of other types of imidazoline compounds.

EXAMPLE 1

1 mol of 1-ethylol-2-heptadecenyl-2-imidazoline was caused to react with 1 mol of methyl acrylate for 3 hours at 80° C. in an aqueous medium in the presence of an alkali catalyst and the product was hydrolyzed to give the sodium salt of 1-carboxyethoxyethyl-2-heptadecenyl-2-imidazoline. Using this salt, the following composition was prepared:

Composition:	Weight percent
Sodium salt of 1-carboxyethoxyethyl - 2 - heptadecenyl-2-imidazoline	20
Mineral oil	60
Polyoxyethylene lauryl ether	10
Sodium salt of petroleum sulfonate	20

The particle size of the thus obtained emulsion in water was less than 0.2 micron and when the emulsion was allowed to stand for 1 week at room temperature, neither creaming nor settling occurred. The above composition was applied to nylon filaments in the form of a 10% emulsion in water in an amount of 0.3% by weight based on the dry weight of the filaments. The antistatic electricity property of thus treated filaments was as follows:

	Electrified potential (volts)
Non treated yarns	+40,000
Treated yarns	−5

In the test, the electrified potential was measured by means of a Kasuga-type electron collecting potentiometer at a moving speed of the filament of 300 m./min. Twenty filaments were tested in one test as a yarn and the measuring conditions were 40% RH and 20° C.

EXAMPLE 2

Component:	Weight percent
Sodium salt of 1-carboxyethoxyethyl - 2 - heptadecenyl-2-imidazoline	20
Octyl oleate	50
Polyoxyethylenated castor oil	25
Oleyl alcohol	5

The antistatic effect in the case of treating polyester filaments by using the above composition was measured. For comparison purposes, the result obtained by testing the same filaments treated by a conventional lubricating oil composition consisting of a mineral oil and polyoxyethylene alkyl ether is also listed.

	Electrified potential (volts)
Non treated filaments	+45,000
Filament treated by the conventional lubricating oil composition	+5,500
Filaments treated by the composition of this invention	+50

EXAMPLE 3

100 parts of sorbitan trioleate and sorbitan monooleate (1:1) were emulsified by the carboxylated imidazoline salt in Example 1 according to this invention and a very stable emulsion was obtained by using 30–40 parts of the imidazoline salt, while a stable emulsion was not obtained by using the acetate of Amine 220 or Miranol CM. This is shown in the following table.

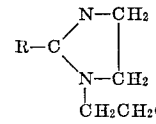
Component:	Average emulsion stability [1] (particle size in microns)
Sorbitan ester (100 parts)/ carboxylated imidazoline (30 parts)	Very stable (0.1).
Sorbitan ester (100 parts)/ Amine 220 Acetate (40 parts)	Unstable (4).
Sorbitan ester (100 parts)/ Miranol CM (40 parts)	Very unstable (10).

[1] As measured by settling state after allowing to stand for 24 hours at 30° C. 100 ml. of the 10% emulsion in a measuring cylinder.

EXAMPLE 4

Antistatic effects were compared by measuring an electrified potential generated when a yarn prepared by depositing on nylon filaments of 210 d./34 0.5% (on the dry weight of fibers) of a lubricant oil composition obtained by mixing 50% of a mineral oil, 30% of a polyoxyethylene oleylether ($\bar{p}$=6) and 20% of an imidazoline compound having the following structural Formula I was moved running in frictional contact with a metallic guide, the result being as follows:

STRUCTURAL FORMULA I



R	Electrified potential, volts	Frictional force, in g.
$C_{11}H_{23}$	−120	55
$C_{15}H_{31}$	−150	56
$C_{17}H_{35}$	−340	53
$C_{17}H_{33}$	−100	50
Coconut alkyl	−140	55
Untreated	+4,000	250

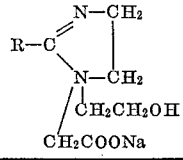
EXAMPLE 5

The substituted imidazoline salt used in the lubricant composition of the present invention could be obtained by hydrolyzing and saponifying a product obtained by reacting methyl acrylate with a 1-ethylol-2-alkyl-2-imidazoline obtained by condensing aminoethyl ethanol with a saturated or unsaturated fatty acid (C_9 to C_{23}, preferably C_{12} to C_{18}) and has the above structural Formula I. Now, for the purpose of comparison, substituted imidazoline compounds having the following structural Formula II obtained by making monochloracetic acid or sodium monochloracetate react at 1:1 mol on 1-ethylol-2-alkyl-2-imidazolines were compared with the imidazoline compounds of the present invention having the above structural Formula I on their antistatic effects.

The test results of the antistatic effects by the use of the lubricant compositions which were made by adding

20% of the respective imidazoline compound having the above structural Formulas I or II to 50% of mineral oil and 30% of polyoxyethylene coconut alkylether ($\bar{p}$=5) were shown in the following table (the treating conditions being the same as in Example 4).

STRUCTURAL FORMULA II



R	Electrified potential, volts	Frictional force, in g.
$C_{11}H_{23}$:		
(I)	−110	54
(II)	−320	50
$C_{17}H_{35}$:		
(I)	−320	52
(II)	−500	47
$C_{17}H_{33}$:		
(I)	−90	49
(II)	−300	48
Untreated	+4,000	250

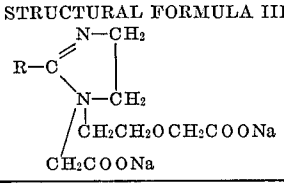
It is apparent that the imidazoline compounds (I) of the present invention are superior in their antistatic effects to the imidazoline compounds (II).

EXAMPLE 6

For the purpose of comparison, substituted imidazoline compounds having the following structural Formula III obtained by making monochloracetic acid or sodium monochloracetate (2 mols) react on 1-ethylol-2-alkyl-2-imidazolines (1 mol) were compared with the imidazoline compounds of the present invention having the above structural Formula I on their antistatic effects.

That is to say, 0.5% on the fiber weight of a mixture obtained by mixing together 55% of mineral oil, 35% of polyoxyethylene coconut alkylester ($\bar{p}$=10) and 20% of the respective imidazoline compound having the structural Formulas I or III was deposited on nylon filaments to prepare a yarn, the electrified potential generated when the yarn was moved running at 300 m./min. while in frictional contact with a metallic guide was measured and the frictional force when it was moved running at 100 m./min. was measured so as to determine the ratio of variation of frictional force at relative humidities of 40 and 90%, the results being as follows:

STRUCTURAL FORMULA III



R	Electrified potential, volts	Frictional force, variation ratio, percent
$C_{11}H_{23}$:		
(I)	−120	6
(III)	−250	10
$C_{17}H_{33}$:		
(I)	−110	7
(III)	−450	10

Frictional force variation ration (in %) =

$$\frac{\text{Frictional force (at 90% R.H.)} - \text{Frictional force (at 40% R.H.)}}{\text{Frictional force (at 40% R.H.)}} \times 100$$

It is apparent that the imidazoline compounds (I) of the present invention are superior in their antistatic effects to the imidazoline compounds (III) and are small in their frictional force variation ratio due to the change of relative humidity compared to the imidazoline compounds (III).

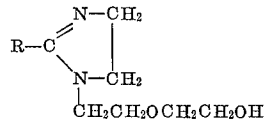
In the following Examples 7 to 10, the carboxylated imidazoline compounds of the present invention were compared with polyoxyethylated imidazoline compounds and sulfated imidazoline compounds on their antistatic effects and other properties.

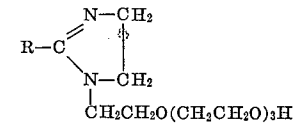
EXAMPLE 7

Since the antistatic agent to be used for a lubricant composition for synthetic fibers is used in combination with a smoothing agent and emulsifying agent, though it is essentially required to be excellent in its antistatic effect, it is further required in the actual use to have an excellent emulsion stability and spreadability on oiling rolls.

For the purpose of comparison, lubricant compositions were made by mixing 50 parts of mineral oil, 10 parts of polyoxyethylene oleylether ($\bar{p}$=6) and 25 parts of sulfated oleyl oleate sodium salt with 15 parts of 1-polyoxyethylene-2-heptadecenyl-2-imidazoline (p=2) having the following structural Formula IV or V obtained by adding respectively 1 and 3 mols of ethylene oxide to 1-ethylol-2-heptadecenylalkyl-2-imidazoline. These respective oil compositions was applied to nylon multifilaments of 210d./34, by setting oiling rolls so as to deposit 0.5% (on the fiber weight) of the composition on said filaments. The spreadability of a 5% solution of the lubricant composition on the oiling rolls, its emulsion stability and the potential generated when the treated yarn was brought into frictional contact with a metallic guide at a yarn velocity of 300 m./min. were measured.

STRUCTURAL FORMULAS





Kinds of imidazoline derivatives	Emulsion stability	Roller wetting	Electrified potential, volts
1-polyoxyethylene-2-heptadecenyl-2-imidazoline ($\bar{p}$=2) of structural formula (IV)	Unstable		
1-polyoxyethylene-2-heptadecenyl-2-imidazoline ($\bar{p}$=4) of structural formula (V)	Stable	Bad	
1-carboxyethoxyethyl-2-heptadecenyl-2-imidazoline of structural formula (I)	do	Good	60

It is apparent that the polyoxyethylenated imidazoline compounds of the structural Formulas IV and V are inferior in the emulsion stability and oiling roller wetting ability or spreadability on oiling rollers to the carboxylated imidazoline compound of the present invention of the structural Formula I.

EXAMPLE 8

The emulsion stability, roller wetting ability and electrified potential when lubricant compositions prepared by mixing 50 parts of mineral oil, 15 parts of a polyoxyethylene cocoalkylether ($\bar{p}$=5), 25 parts of sulfated whale oil and 10 parts of respective kinds of imidazoline compounds were used were measured by the same method as in Example 8 and the following results were obtained.

Kinds of imidazoline compounds	Emulsion stability	Roller wetting	Electrified, potential volts
1-1-polyoxyethylene-2-heptadecenyl-2-imidazoline ($\bar{p}$=2)	Stable	Good	500
1-carboxyethoxyethyl-2-heptadecenyl-imidazoline-(2)	do	do	100

EXAMPLE 9

In the same manner as in Example 7, 0.7% of respective lubricant composition prepared by mixing 50 parts of mineral oil, 35 parts of polyoxyethylene cocoalkylester ($\bar{p}$=10), 10 parts of sulfated butyl oleate sodium salt and 5 parts of respective imidazoline compound was deposited on fibers and the electrified potential was measured by the same method as in Example 1 and the following results were obtained.

Kinds of imidazoline derivatives	Emulsion stability	Roller wetting	Electrified potential, volts
1-polyoxyethylene-2-heptadecenyl-2-imidazoline (p=4)	Stable	Good	−800
1-ethylolcarboxyethylether-2-heptadecenyl-2-imidazoline	do	do	70

It is apparent that the carboxylated imidazoline compound of the present invention could give a lubricant composition having an antistatic property higher than of polyoxyethylenated imidazoline compound and also higher in the emulsion stability and the spreadability (wetting) on oiling rollers which are essentially required for a fiber treating oil composition.

EXAMPLE 10

105 mols of chlorosulfonic acid were dropped at 15 to 20° C. in a trichlorethylene solvent into 1 mol of 1-ethylol-2-heptadecenyl-2-imidazoline to cause a sulfating reaction. The solution was neutralized with a 20% caustic soda solution and was then filtered to remove the solvent. The following lubricant compositions were prepared by using the thus obtained 1-ethylol-2-heptadecenyl-imidazoline sulfate salt (which shall be briefly called a sulfated imidazoline compound hereinbelow) and the carboxylated imidazoline compound of the present invention, respectively, and 0.5% of each of them was deposited on nylon multifilaments of 210 d./34. (The generated potentials at 300 m./min. were measured to compare their antistatic activities and other properties were also measured.)

Composition:	Percent
Mineral oil	30
Butyl stearate ester	20
Polyoxyethylene oleyl alcohol ester ($\bar{p}$=10)	30
Imidazoline derivative	20

Kinds of imidazoline derivatives	Emulsion stability	Roller wetting	Electrified potential, volts
1-carboxyethoxyethyl-2-heptadecyl-2-imidazoline	Stable	Good	70
Sulfated imidazoline	do	do	400

The following Examples 11–16 are examples of the present invention in which various fatty acid esters were used as lubricant component.

EXAMPLE 11

Nylon was treated with 0.7% of a mixed composition obtained by first mixing 30 parts of a refined mineral oil of a viscosity of 400 seconds by Redwood with 20 parts of a fatty acid ester obtained by making 1 mol of a soybean oil fatty acid react at 230° C. for 5 hours in the presence of a tin catalyst on 1 mol of coconut alcohol derived from coconut oil and then adding 30 parts of a polyoxyethylene oleylester ($\bar{p}$=10) and 20 parts of 1-carboxyethoxyethyl-2-heptadecenyl-2-imidazoline and was run while in frictional contact with a metallic guide and the generated potential was measured to obtain the following results.

Electrified potential, volts

Untreated yarn	+40,000
Treated yarn	+120

EXAMPLE 12

A nylon yarn was treated with 0.7% of a mixed composition obtained by mixing 30 parts of polyoxyethylene hardened castor oil ($\bar{p}$=25), 15 parts of 1-carboxyethoxyethyl-2-heptadecenyl-2-imidazoline and 5 parts of sodium dodecylsulfonate with 50 parts of a fatty acid ester obtained by making 1 mol of castor oil fatty acid react on 1.05 mol of the above mentioned coconut alcohol at 230° C. for 5 hours in the presence of a tin catalyst and was run while in frictional contact with a metallic guide and the generated potential at 300 m./min. was measured.

Electrified potential, volts

Untreated yarn	+40,000
Treated yarn	+370

EXAMPLE 13

Nylon was treated with 0.7% of a mixed composition obtained by mixing 20 parts of polyoxyethylene castor oil ($\bar{p}$=15), 20 parts of a mineral oil of a viscosity of 100 seconds by Redwood, 40 parts of a polyoxyethylene alkyl ester ($\bar{p}$=15), 15 parts of 1 - carboxyethoxyethyl - 2-heptadecyl-2-imidazoline and 5 parts of oleyl alcohol sulfate with 30 parts of coconut monoglyceride derived from coconut oil and was run while in frictional contact with a metallic guide and the generated potential was measured.

Electrified potential, volts

Untreated yarn	+40,000
Treated yarn	+320

EXAMPLE 14

0.5% of a mixed oil composition obtained by adding 30 parts of polyoxyethylene castor oil ($\bar{p}$=50) and 5 parts of 1-carboxyethoxyethyl-2-octadecyl imidazoline to 65 parts of diolein obtained by making 1 mol of oleic acid and 2 mols of glycerin react with each other at 230° C. for 5 hours in the presence of a tin catalyst was deposited on nylon, the nylon was run while in frictional contact with a metallic guide and the generated potential was measured.

Electrified potential, volts

Untreated yarn	+40,000
Treated yarn	+250

EXAMPLE 15

0.5% of a mixed composition obtained by mixing 30 parts of polyoxyethylene oleate ($\bar{p}$=10), 15 parts of 1-carboxyethoxyethyl - 2 - heptadecyl-2-imidazoline and 5 parts of sulfated oleate with 50 parts of an adipate obtained by adding 2 mols of coconut alcohol to 1 mol of adipic acid to react under a sulfuric acid catalyst under reflux with benzene was deposited on nylon and the nylon was run at 300 m./min. while in frictional contact with a metallic guide and the potential generated in such case was measured.

Electrified potential, volts

Untreated yarn	+40,000
Treated yarn	−300

EXAMPLE 16

1.0% of a mixed composition obtained by mixing 30 parts of a mineral oil of a viscosity of 60 seconds by Redwood, 30 parts of polyoxyethylene coconut fatty acid ester and 10 parts of 1-carboxyethoxyethyl-2-heptadecenyl-2-imidazoline with 30 parts of a sebacate obtained by adding 2 mols of 2-ethylhexanol to 1 mol of sebacic acid to react at 120° C. under a para-toluene-sulfonic acid catalyst under reflux with benzene was deposited on nylon and the nylon was run at 300 m./min. while in frictional contact with a metallic guide and the potential generated was measured.

Electrified potential, volts

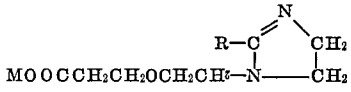
Untreated yarn	+40,000
Treated yarn	+200

As shown in the above examples, the lubricating oil composition for synthetic fibers of this invention forms

easily a stable emulsion and the antistatic effect is very excellent even in conditions of low relative humidity. Further, the composition of this invention is by no means inferior to coventional lubricants as far as reducing yarn to yarn friction or yarn to metal friction is concerned.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An antistatic lubricant composition for synthetic fibers consisting essentially of (1) 10–50% by weight of a substituted imidazoline of the formula:



wherein R is an alkyl or alkenyl group containing from 8 to 22 carbon atoms and M is an alkali metal, and (2) 40–80% by weight of a lubricating component selected from the group consisting of a mineral oil and an ester selected from the group consisting of (a) esters of saturated and unsaturated fatty acids containing from 6 to 22 carbon atoms with saturated and unsaturated monohydric aliphatic alcohols containing from 6 to 22 carbon atoms, (b) glycerine monoesters and diesters of saturated and unsaturated fatty acids containing from 6 to 22 carbon atoms, and (c) esters of dicarboxylic aliphatic acids containing from 6 to 10 carbon atoms with saturated and unsaturated monohydric aliphatic alcohols containing from 6 to 13 carbon atoms.

2. An antistatic lubricant composition as claimed in claim 1, in which R contains 11–17 carbon atoms.

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HERBERT B. GUYNN, Primary Examiner

U.S. Cl. X.R.

117—138.8, 139.5; 252—8.6, 8.75; 260—309.6