

1

3,277,079

ORGANIC COMPLEX FOR USE AS AN ANTI-STATIC AGENT

Jack J. Press, 12-18 E. Laurelton Parkway, Teaneck, N.J.
No Drawing. Filed Jan. 29, 1964, Ser. No. 341,136
7 Claims. (Cl. 260-232)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention in general relates to the treatment of polymeric materials such as textiles and the like for the purpose of providing a finish on such material. More particularly, this invention relates to a new class of organic complexes for use in treating polymeric material in order to impart a durable anti-static quality to the material and to increase its soil resistance.

It is well known that static electricity may be generated by textiles during processing. It can be generated in the blending and carding operation down through the drawing, sizing, knitting or weaving operation, or even in the final operation of inspection and packing. It is well known that static electricity, when generated, can result in a myriad number of potential difficulties to the manufacturer such as a reduction in output, a lowering of quality, an increase in waste, and a hazard to personnel. Industry has recognized the aforementioned difficulties and has attempted to prevent textiles from generating static electricity by applying anti-static agents to the surface of the textile in the form of finishes and coatings.

To date, cationic surface active agents are considered to be one of the most effective materials known for their ability to impart anti-static qualities to textiles. However, there are a number of serious limitations encountered in the use of these agents. For instance, they are generally soft and waxy and are likely to impart only a temporary finish to the textile because they are quite easily rubbed off or washed from the treated surface. Another difficulty lies in the fact that the treated surfaces are easily soiled. A further difficulty is attributable to the development of many new fibers and blends of fibers and the fact that the affinity and efficiency of the cationic surface-active agent varies from surface to surface.

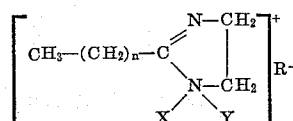
Attempts have been made to overcome the deficiencies encountered in the use of cationic surface active agents by chemically altering the surface of the textile in order to enhance the affinity of the surface towards the cationic surface active agent. For example, polymeric materials have been insolubilized on the surface of the textile in an effort to increase the affinity of the surface for the surface active agents which are usually applied in a subsequent treatment. However, such attempts are complicated and have limited application. For instance, the activity of the surface active agent is limited to interaction with the external surface of the coating. As a result, the new-external layer of surface active agent is directly exposed and readily removed by rubbing and washing.

I have now discovered a new class of organic complexes which may be used to treat textile fibers, yarns, fabrics and the like to give solid coatings of exceptional anti-static quality. When these complexes are in the dispersed form, they exhibit excellent spreading characteristics. It is also possible to apply a dispersion of the complex to a textile in a one stage process due to the fact that the dispersion may exist as a concentrated solution of low-viscosity. The coatings which result from the use of these complexes exhibit excellent adhesion, good dimensional stability under both moist and dry conditions, and exceptional durability to mechanical wear. Added ad-

2

vantages lie in the fact that these complexes are comparatively less water soluble and do not require a heat treatment to insolubilize them on the treated textile.

The composition of this invention consists essentially of an organic complex resulting from the interaction of a fatty imidazoline or imidazolinium compound with a dispersed homo or copolymer containing a plurality of acidic groups. The formula for the complex is as follows:



wherein R represents a water soluble or dispersed acidic polymer or salt thereof prepared by oxidation, carboxylation, phosphorylation, or sulfonation; X represents either an alkanol or alkyl group having 1 to 4 carbon atoms; Y represents either hydrogen or an alkyl group having 1 to 4 carbon atoms; and n is an integer from 6 to 18.

The imidazoline or imidazolinium compounds which may be used to produce the aforementioned complex include oleyl imidazoline, lauryl imidazoline, stearyl imidazoline, and stearyl imidazolinium chloride.

The soluble or dispersible polymers which may be used in preparing the aforesaid complex include sodium carboxymethyl cellulose, sodium phosphated cellulose, and sodium sulphonated cellulose. These are used in proportion to the imidazoline in a molar ratio of 1:1 to 10:1.

The dispersed organic complex of this invention may be readily applied to a fabric by a simple dipping, coating, spraying or wiping application. The resulting protective coatings have good adhesion and durability and confer new surface characteristics such as static resistance and soil resistance.

The following are examples of the general method of preparation of some representative organic complexes which fall under the broad concept of this invention. Each of these examples is followed by an illustration of the results encountered when the organic complex is applied to some polymeric material.

EXAMPLE 1

5 grams of oleyl imidazoline having a molecular weight of about 355 are dissolved in 100 mls. of water. The pH of the solution is brought to about 7 with acetic acid and the resultant solution is diluted in order to obtain a 1% solution of imidazoline in water. 50 ml. of a 1% water solution of sodium carboxymethyl cellulose are then added to 15 ml. of the above 1% imidazoline solution to give 65 ml. of a 1% complex solution at about a 5 to 1 molar ratio. The carboxymethyl cellulose utilized had an equivalent molecular weight per carboxy group of about 320 and 0.7 carboxyether groups per anhydroglucose unit.

EXAMPLE 2

The complex was prepared in accordance with the procedure outlined in Example 1 except, in this case, the sodium carboxymethyl cellulose utilized had an equivalent molecular weight per carboxy group of about 220 and 1.2 carboxy ether groups per anhydroglucose unit.

Application

Individual fabrics made either of low density polyethylene or high density polypropylene were cut into strips 4" x 6" in size, dipped in one of the treat solutions prepared in accordance with the indicated procedure heretofore outlined, drained and dried at 180° F. The treated samples were then tested for static resistance by testing

3

for resistivity at 70° F. and 65% relative humidity and the results are set forth below:

TABLE 1

Treat	Resistivity ($\times 10^{10}$ ohms/sq. in.)	
	Polyethylene	Polypropylene
Blank.....	25,000	20,000
Ex. 1.....	0.04	0.2
Ex. 2.....	0.25	0.2

NOTE.—In each case where the samples were treated with a complex prepared in accordance with this invention, the static propensity of the treated sample was drastically reduced when compared to a control sample or blank.

Soiling

In the soiling test, duplicate 2" x 2" squares of each of the samples treated in accordance with the above procedure were placed in a metal launderometer jar together with synthetic soil and metal balls. The jar was rotated at room temperature for 30 minutes. Powdered anhydrous sodium sulfate was added to the jar and the jar was then rotated for an additional 2 minutes. The soiled samples were then removed from the jars and shaken by hand in a screen bottomed pan to remove the excess soil and sodium sulfate and tested for reflectivity.

TABLE 2

Treat	Percent Reflectivity of Soiled Samples	
	Polyethylene	Polypropylene
Blank.....	49	59
Ex. 1.....	70	64
Ex. 2.....	69	61

NOTE.—The samples which had been pretreated with the present complexes exhibited greater reflectivity in all cases which indicates that the treated samples were more soil resistant than the control sample or blank.

Soil removal

To determine the ease of soil removal, the soiled samples prepared in accordance with the above procedure were given three 5 minute rinses at 100° F. in a laundry wash wheel and then were tumble dried. The reflectivity of such treated samples was then taken using a photovolt reflectometer, a tristimulus filter, and black and white standards.

TABLE 3

Treat	Percent Reflectivity of Rinsed Samples	
	Polyethylene	Polypropylene
Blank.....	61	64
Ex. 1.....	71	69
Ex. 2.....	75	71

NOTE.—In each case, the reflectivity of the sample treated with a complex in accordance to this invention is greater than that of a control sample or blank. This indicates that the ease of soil removal is increased by this treatment.

EXAMPLE 3

The complex in this example was prepared in accordance with the procedure outlined in Example 1 except that a proportionate amount (15.2 ml.) of a 1% water solution of stearyl imidazoline having a pH of 7 and molecular weight of 360 was mixed with the 1% water solution of sodium carboxymethyl cellulose in place of oleyl imidazoline.

Application

In accordance with the procedure set forth in Example 3, a batch of the complex dispersion was prepared and applied to a series of fabrics. In this practice, each of the fabrics was dipped into the complex solution, drained well, dried and then tested for electrical resistivity at 70°

4

and 65% relative humidity by the AATCC Test Method 76-1949 which is titled "Electrical Resistivity." The results from the latter test are set forth in the table below.

TABLE 4

	Electrical Resistivity ($\times 10^{10}$ ohms/sq. cm.)			
	Polyethylene	Mylar	Polypropylene	Vinyl
Treated.....	1	1	1	0.6
Control.....	50,000	20,000	100,000	1,000

As shown by the above table, there is a large reduction in resistivity in the case of the treated fabrics when compared to the resistivity of an identical control or untreated fabric.

EXAMPLE 4

11.7 ml. of a 1% water solution of lauryl imidazoline having a pH of 7 and a molecular weight of 276 was mixed with 50 ml. of a 1% water solution of sodium carboxymethyl cellulose in accordance with the procedure outlined in Example 1. The imidazoline solution had been brought to a neutral pH with acetic acid. The cellulose derivative had an equivalent molecular weight per carboxy group of about 320 and about 0.7 carboxyether group per anhydroglucose unit.

Application

The complex solution prepared by the procedure set forth in Example 4 was applied to several different film and fabric samples. These included a woven low density polyethylene monofilament fabric, a water high density isotactic polypropylene monofilament fabric, a polyethylene film, and Mylar polyester film. The samples were each dipped in the complex solution, drained, dried at 160° F. and then conditioned at 70° F. and 65% R.H. The samples were then tested for electrical resistivity and the results were tabulated in the table below.

TABLE 5

	Electrical Resistivity ($\times 10^{10}$ ohms/sq. cm.)			
	Polyethylene Fabric	Polypropylene Fabric	Polyethylene Film	Polyester Film
Treated.....	15	9	5	10
Control.....	25,000	20,000	50,000	20,000

As is evident from the above table, a greater reduction in electrical resistivity is achieved after each of the samples had been treated with the complex solution prepared in accordance with Example 4.

EXAMPLE 5

In this example, the complex was prepared by mixing 19.2 ml. of a 1% water solution of stearyl imidazolinium chloride with 50 ml. of a 1% water solution of sodium carboxymethyl cellulose. The imidazolinium had a molecular weight of 455 and the solution had been neutralized with acetic acid prior to mixing with the cellulose derivative. The carboxymethyl cellulose derivative had an equivalent molecular weight of about 220 and about 1.2 carboxyether groups per anhydroglucose unit.

Application

In this case, a series of fabrics were individually dipped in a complex solution prepared in accordance with Example 5. After a suitable contact period, each of the samples was drained, dried, and conditioned at 70° and 65% R.H. A sample of each the fabrics was then tested for electrical resistivity and the remaining samples were laundered twice in accordance with the Federal Test Methods ccc-191b, method 5556 prior to the resistivity

5

test. The results of such testing are set forth in the table below.

TABLE 6

	Electrical Resistivity ($\times 10^{10}$ ohms/sq. cm.)			
	Nylon	Dacron	Orlon	Dynel
Control.....	600	3,000	4,000	1,000
Treated.....	.06	.01	.01	.01
Treated/Laundered..	6	1.5	8	8

NOTE.—In each case, the electrical resistivity was lowered by a treatment with the complex described and this effect was maintained to a degree even after laundering.

EXAMPLE 6

The complex in this example was prepared by mixing 39.0 ml. of a 1% water solution of sodium phosphated cellulose having an equivalent of molecular weight per phosphate group of 250 with 15 mls. of a 1% water solution of oleyl imidazoline having a molecular weight of 355, the imidazoline solution having been pre-neutralized with acetic acid.

Application

A series of fabric samples were treated with the complex resulting from the procedure outlined in Example 6. Each of the samples was dipped, drained, dried at 70° F. and conditioned at 65% R.H. After treatment, each of the samples was tested for electrical resistivity and the results were tabulated in Table 7 which follows:

TABLE 7

	Electrical Resistivity ($\times 10^{10}$ ohms/sq. cm.)					
	Cotton	Wool	Nylon	Dacron	Orlon	Dynel
Treated.....	0.03	0.01	0.06	0.01	0.01	0.01
Control.....	0.4	100	600	3,000	4,000	1,000

As the results indicate, the treatment is quite effective on a wide variety of fabrics.

EXAMPLE 7

In this example to prepare the complex, 46.9 mls. of a 1% water solution of sodium sulphonated cellulose having an equivalent molecular weight of 300 per sulphonate group was mixed with 15 mls. of a 1% water solution of oleyl imidazoline which had been neutralized with acetic acid as set forth in Example 1.

Application

The complex of Example 7 was used to treat a series of fabrics such as those contained in Table 7 in accordance with the procedures heretofore outlined. The results indicated that this complex is also an effective anti-static agent.

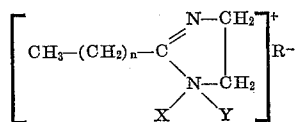
It is quite evident from the results heretofore set forth that the complexes embraced by the broad concept of this invention are quite effective as anti-static agents. Obviously, there are many modifications and variations which are possible in view of the above teaching. For instance, the use of the present complex need not be restricted to

6

fabrics but may be used to impart anti-static resistance to films, plastics, and other non-conducting surfaces. It is to be understood therefore that these modifications and variations are to be included within the scope of the appended claims.

I claim:

1. An organic complex for use as an anti-static agent, said complex having the formula



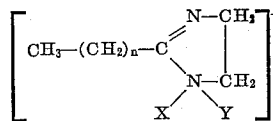
wherein:

- 15 R is selected from the group consisting of an acidic cellulose polymer;
X is hydrogen;
Y is hydrogen; and
n is an integer from 12 to 18.

20 2. The complex of claim 1 wherein

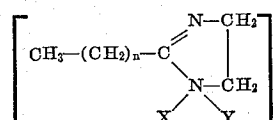
R is selected from the group consisting of sodium carboxymethyl cellulose, sodium phosphated cellulose, and sodium sulphonated cellulose.

25 3. The complex of claim 1 wherein



30 represents an imidazolinium selected from the group consisting of oleyl imidazolinium, lauryl imidazolinium, and stearyl imidazolinium.

35 4. The complex of claim 2 wherein



40 represents an imidazolinium selected from the group consisting of oleyl imidazolinium, lauryl imidazolinium, and stearyl imidazolinium.

45 5. The complex of claim 4 wherein the imidazolinium is a compound selected from the group consisting of oleyl imidazolinium, lauryl imidazolinium, and stearyl imidazolinium and R represents sodium carboxymethyl cellulose.

50 6. The complex of claim 4 wherein the imidazolinium is oleyl imidazolinium and R represents sodium phosphated cellulose.

55 7. The complex of claim 4 wherein the imidazolinium is oleyl imidazolinium and R represents sodium sulphonated cellulose.

References Cited by the Examiner

UNITED STATES PATENTS

2,874,074 2/1959 Johnson 117—139.5

60 LEON J. BERCOVITZ, Primary Examiner.

R. W. MULCAHY, Assistant Examiner.