United States Patent [19]

Tsuji et al.

[11] **3,876,430**

[45] **Apr. 8, 1975**

[54] **ANTISTATIC PHOTOGRAPHIC MATERIAL**

[75] Inventors: **Nobuo Tsuji; Takayuki Inayama; Itsuki Toriya,** all of Kanagawa, Japan

[73] Assignee: **Fuji Photo Film Co., Ltd.,** Kanagawa, Japan

[22] Filed: **Mar. 22, 1974**

[21] Appl. No.: **453,893**

[30] **Foreign Application Priority Data**

Mar. 22, 1973 Japan 48-32837

[52] **U.S. Cl.** .... **96/87 A;** 96/114.2
[51] **Int. Cl.** **G03c 1/82**
[58] **Field of Search** .... 96/87 A, 114.2, 84 R

[56] **References Cited**

UNITED STATES PATENTS

3,271,148	9/1966	Whitmore	96/84 A
3,671,468	6/1972	Tsuda et al.	260/2 R
3,794,495	2/1974	Ishihara et al.	96/87 A
3,811,887	5/1974	Ishihara et al.	96/87 A

Primary Examiner—Ronald H. Smith
Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn and Macpeak

[57] **ABSTRACT**

An antistatic photographic material containing an antistatic compound derived from a diamine and a bis-(haloacetyl) glycol in at least one of the layers of the photographic material. The formation of static marks can be prevented even at low humidity.

4 Claims, No Drawings

ANTISTATIC PHOTOGRAPHIC MATERIAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an antistatic photographic film, and more specifically, to an antistatic photographic material comprising at least one photographic silver halide emulsion layer and at least one antistatic layer.

2. Description of the Prior Art

Static charges tend to build up during the manufacture and use of photographic films. In the manufacturing process, static charges are generated, for example, in the contact part between the photographic film and the roll, or by friction between the support surface and the emulsion layer during winding or unwinding the photographic film or by the peeling off of the emulsion layer from contact with a support. In use, it is generated and then discharged by the peeling away of the emulsion layer of one section of the film from contact with the support of an other section of the film when the film is exposed to a high humidity causing blocking of the film. Static charges are also generated when a motion picture camera or an automatic developing machine for X-ray films is used. Films are exposed when the built-up static charges are discharged, and after development, irregular static marks in the form of, for example, a blot, a tree branch, or a feather are formed on the films to decrease their commercial value drastically. This problem is troublesome since such static marks cannot be discerned until the films are developed. The built-up static charges cause the adhesion of dirt and dust to the surface of films, and secondary difficulties such as nonuniformity of coating result. Furthermore, since all film supports are hydrophobic, the build-up of static charge is remarkable. Thus, the occurrence of static marks increases with the increase in the speed of processing and the sensitivity of the emulsion, and exerts adverse effects.

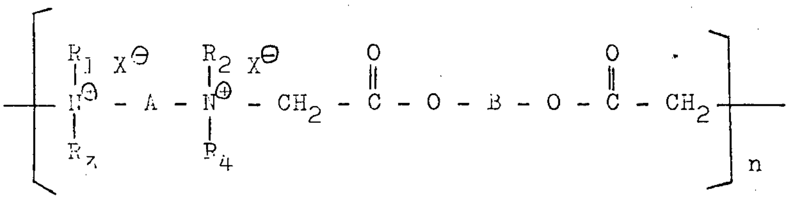
Various substances have been used previously in an attempt to prevent formation of static charges on photographic films. These substances are ionic conductive substances or hygroscopic substances, and are used, either alone or in combination, to impart electric conductivity to films and dissipate electric charges quickly before discharge occurs due to the build-up of electric charges. In order to impart antistatic prevention directly to a support of a photographic film, it is known to incorporate such a substance directly in a polymeric substance which forms the support, or coat it on the surface of the support. Where the agent is coated on the surface of the support, the antistatic agent is coated either alone or in admixture with a polymeric substance such as gelatin, polyvinyl alcohol, or cellulose acetate. The antistatic agent can also be added to a photographic emulsion layer formed on the support or to a non-sensitive auxiliary layer (for example, a backing layer, anti-halation layer, interlayer, or protective layer). Alternatively, the anti-static agent can be coated on the film after development in order to prevent the adhesion of dirt and dust during the handling of the developed film.

Known antistatic agents do not exhibit satisfactory effects on photographic materials having an emulsion layer with high sensitivity, especially under low humidity conditions. In addition, the antistatic effects frequently decrease with the passage of time, and also adhesion difficulties are frequently caused under high temperature high humidity conditions. Furthermore, the antistatic agents sometimes adversely affect the photographic properties of photographic materials, and therefore have been difficult to apply to photographic materials. Accordingly, attempts have been made to employ various antistatic agents for photographic materials.

It is an object of this invention to provide an antistatic agent suitable for obtaining a photographic material of markedly reduced tendency for static charges to form without adversely affecting the photographic characteristics of the material.

SUMMARY OF THE INVENTION

We have found that good antistatic effects can be obtained by incorporating a compound of the following formula



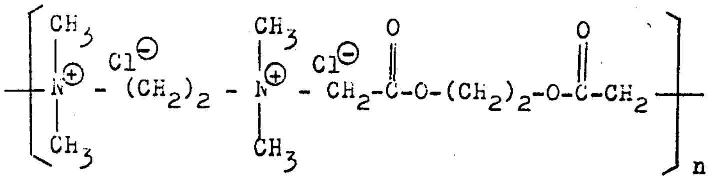
$$-\!\left[\overset{R_1\ X^{\ominus}}{\underset{R_3}{N^{\oplus}}} - A - \overset{R_2\ X^{\ominus}}{\underset{R_4}{N^{\oplus}}} - CH_2 - \overset{\overset{O}{\|}}{C} - O - B - O - \overset{\overset{O}{\|}}{C} - CH_2\right]_n\!-$$

in one of the layers of a photographic material.

In the above formula, A and B (e.g., having 2 to 10 carbon atoms) each represent a straight chain or branched chain alkylene, xylylene or cyclohexylene group, and the straight chain or branched chain alkylene group may contain a double bond, triple bond or a $-(CH_2CH_2O)_n-CH_2-CH_2-$ group in the alkylene chain; R_1, R_2, R_3 and R_4 each represent a lower alkyl group (e.g., having 1 to 3 carbon atoms), or R_1 and R_2 and/or R_3 and R_4 each may be bonded to form a nitrogen-containing heterocyclic ring; X is anion; n is an integer of about 20 to 50; and X is any anion which balances the charge of the positively charged nitrogen atom, and preferably is a halogen ion (e.g., chlorine, bromine or iodine).

Specific examples of compounds of the above formula are given below. The intrinsic viscosities [η] were measured in a 0.05 M NaCl aqueous solution at 24.7° ± 0.02°C using a modified Ostwald viscometer. A suitable intrinsic viscosity range is from about 0.01 to 0.8, preferably 0.05 to 0.3.

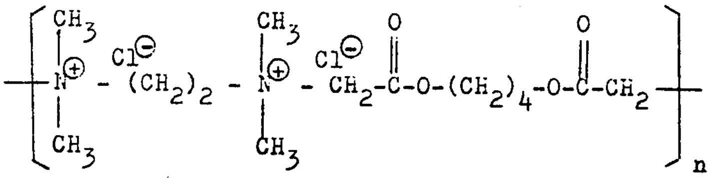
1



$$\left[-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^{\oplus}}}\overset{Cl^{\ominus}}{-}(CH_2)_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^{\oplus}}}\overset{Cl^{\ominus}}{-}CH_2-\overset{\overset{O}{\|}}{C}-O-(CH_2)_2-O-\overset{\overset{O}{\|}}{C}-CH_2-\right]_n$$

$[\eta] = 0.07$

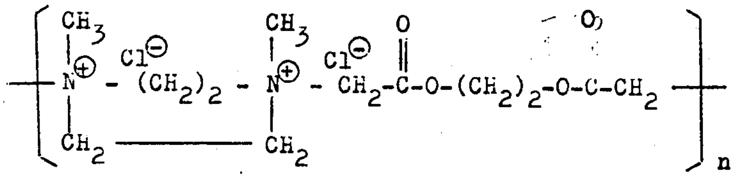
2



$$\left[-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^{\oplus}}}\overset{Cl^{\ominus}}{-}(CH_2)_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^{\oplus}}}\overset{Cl^{\ominus}}{-}CH_2-\overset{\overset{O}{\|}}{C}-O-(CH_2)_4-O-\overset{\overset{O}{\|}}{C}-CH_2-\right]_n$$

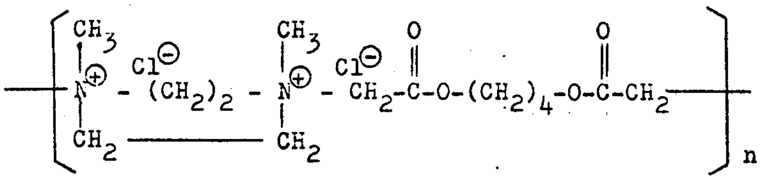
$[\eta] = 0.10$

3



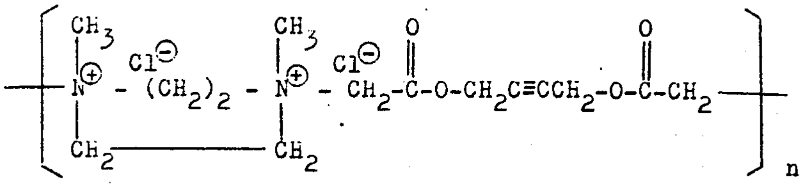
$[\eta] = 0.10$

4



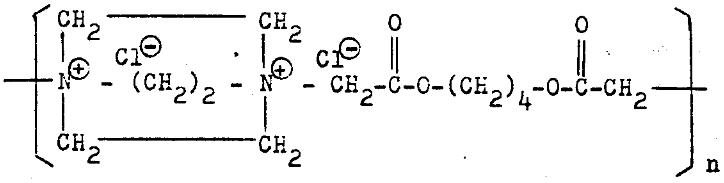
$[\eta] = 0.07$

5



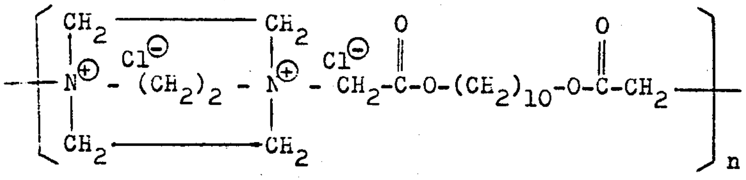
$[\eta] = 0.12$

6



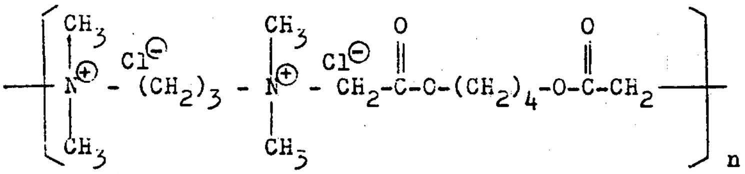
[η] = 0.10

7



[η] = 0.12

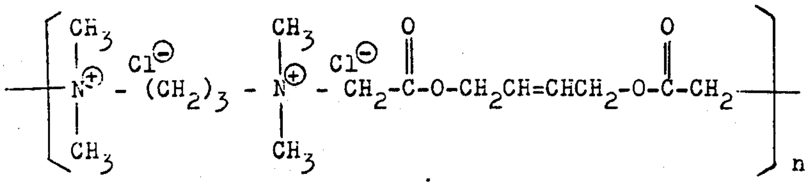
8



$$\left[-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}} \overset{Cl^{\ominus}}{-} (CH_2)_3 - \overset{CH_3}{\underset{CH_3}{N^{\oplus}}} \overset{Cl^{\ominus}}{-} CH_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-CH_2- \right]_n$$

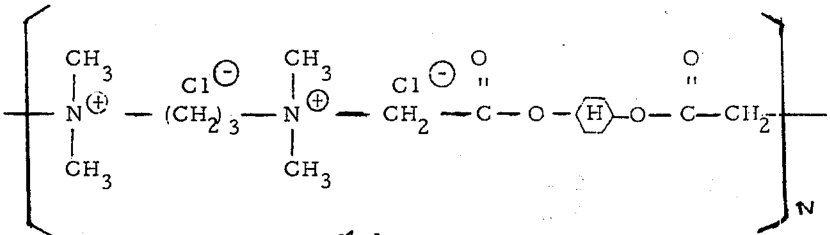
[η] = 0.09

9



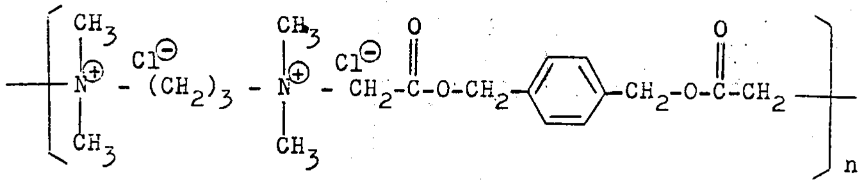
$$\left[-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}} \overset{Cl^{\ominus}}{-} (CH_2)_3 - \overset{CH_3}{\underset{CH_3}{N^{\oplus}}} \overset{Cl^{\ominus}}{-} CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2CH{=}CHCH_2-O-\overset{O}{\overset{\|}{C}}-CH_2- \right]_n$$

[η] = 0.13



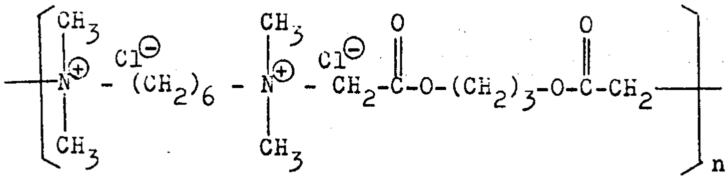
[η] = 0.09

11



$[\eta] = 0.21$

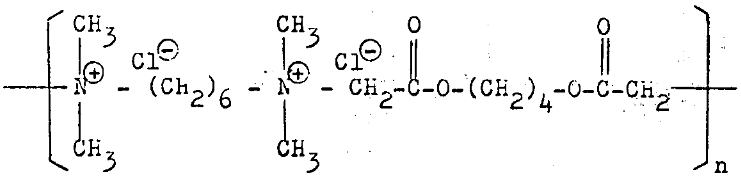
12



$$\left[-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}\;Cl^{\ominus}-(CH_2)_6-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}\;Cl^{\ominus}-CH_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_3-O-\overset{O}{\overset{\|}{C}}-CH_2-\right]_n$$

$[\eta] = 0.14$

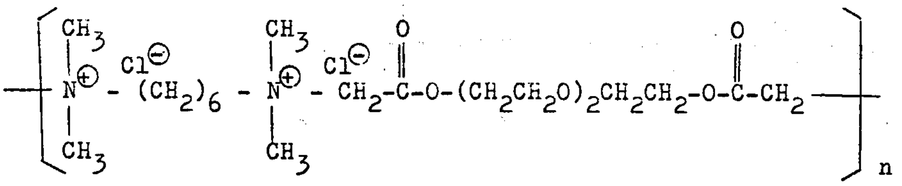
13



$$\left[-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}\;Cl^{\ominus}-(CH_2)_6-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}\;Cl^{\ominus}-CH_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-CH_2-\right]_n$$

$[\eta] = 0.23$

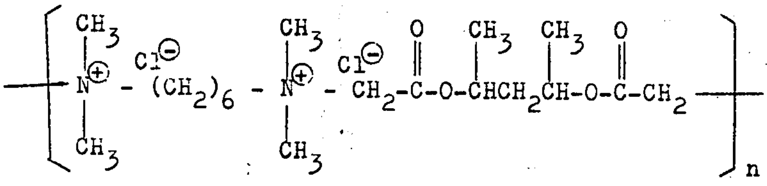
14



$$\left[-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}\;Cl^{\ominus}-(CH_2)_6-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}\;Cl^{\ominus}-CH_2-\overset{O}{\overset{\|}{C}}-O-(CH_2CH_2O)_2CH_2CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-\right]_n$$

$[\eta] = 0.16$

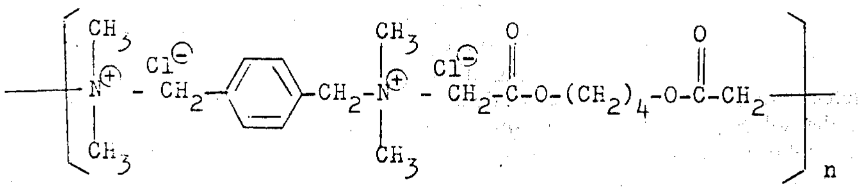
15



$$\left[-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}\;Cl^{\ominus}-(CH_2)_6-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}\;Cl^{\ominus}-CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{\overset{|}{C}}HCH_2\overset{CH_3}{\overset{|}{C}}H-O-\overset{O}{\overset{\|}{C}}-CH_2-\right]_n$$

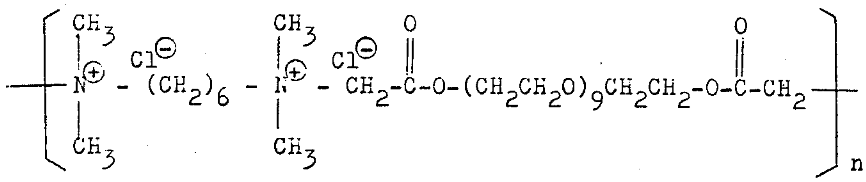
$[\eta] = 0.12$

16



$[\eta] = 0.17$

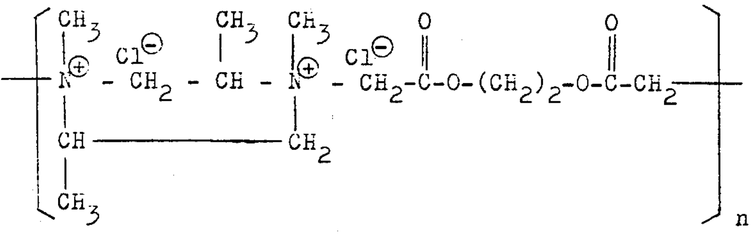
17



$$\left[-\underset{CH_3}{\overset{CH_3}{N^{\oplus}}}\;Cl^{\ominus} - (CH_2)_6 - \underset{CH_3}{\overset{CH_3}{N^{\oplus}}}\;Cl^{\ominus} - CH_2-\overset{O}{\overset{\|}{C}}-O-(CH_2CH_2O)_9CH_2CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2- \right]_n$$

$[\eta] = 0.17$

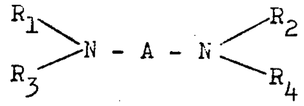
18



$[\eta] = 0.15$

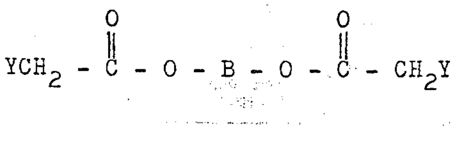
According to this invention, static marks which tend to occur when loading a film in a camera or removing a film from a film case at the time of development can be effectively prevented even at low humidity, and the antistatic effects are not reduced with the passage of time. Furthermore, the antistatic compound used in this invention does not adversely affect the photographic properties, such as sensitivity, gamma, or fog.

The compounds used in this invention can be synthesized by reacting diamines of the formula (II)



(II)

wherein R_1, R_2, R_3, R_4 and A are the same as defined above, with bis-haloacetyl) glycols of the formula (III)



$$YCH_2-\overset{O}{\overset{\|}{C}}-O-B-O-\overset{O}{\overset{\|}{C}}-CH_2Y \qquad (III)$$

wherein Y is a halogen atom (as above), and B is the same as defined above. Examples of compounds of formula (II) are 1,4-dimethylpiperadine, triethylene diamine, N,N,N',N'-tetramethyl ethylenediamine, N,N,N', N'-tetramethyl propylenediamine, N,N,N', N'-tetramethylhexamethylenediamine, and N,N,N', N'-tetramethyl xylylenediamine, and other analogous compounds. Examples of compounds of formula (III) include bis-(chloroacetyl)-ethylene glycol, bis(-chloroacetyl)-1,4-butanediol, bis-(chloroacetyl)-1,3-propanediol, bis-(chloroacetyl)-1,10-decanediol, bis-(chloroacetyl)-cyclohexanediol, bis-(chloroacetyl)xyleneglycol, bis-(chloroacetyl)-butenediol, bis-(chloroacetyl)butenediol, bis-(chloroacetyl) polyethylene glycol, and other analogous compounds.

Details of the method of synthesis are given, for example, in U.S. Pat. No. 3,671,468.

One example of the method of synthesis is given below. Unless otherwise indicated, all parts, percents, ratios and the like given herein are by weight.

11.5 g of 1,4-dimethylpiperadine was dissolved in 100 ml of benzene, and 25.5 g of bis-(chloroacetyl)-ethylene glycol was added to the solution, followed by heating the mixture with stirring. After about 10 minutes, a white viscous substance began to precipitate and the viscosity of the solution increased, thereby making it extremely difficult to stir the solution. In about 30 minutes, the reaction was completed. After cooling, the precipitate was separated from the solvent, and dissolved in methanol. The resultant solution was added dropwise to diethyl ether to obtain a precipitate. The resulting purified product was a highly hydroscopic white polymer. The amount of the polymer yield was 25.5 g, and the intrinsic viscosity $[\eta]$ of the polymer was 0.10 measured as described above.

The amount of the compound used in this invention varies according to the type of photographic material used, its form, the method of coating, etc. The compound can be present in a layer of the photographic material. Generally, however, it is advisable to incorporate the compound in a surface layer in an amount of 0.01 to 1.0 g, especially 0.03 to 0.4 g, per square meter of the photographic film. Suitable examples of photographic materials include black and white films, X-ray films, lithographic films, cine films, color papers, color films, etc.

Prior to applying the antistatic compound of this invention to a photographic film, it is dissolved in water, an organic solvent such as methanol or acetone or a mixture of an organic solvent and water. A suitable concentration ranges from about 0.05 to 0.5% by weight with a suitable concentration being about 3 to 20% by weight to the binder. Then, the resulting solution is sprayed or coated on the surface of the support or emulsion layer of the film, or the film is immersed in the solution and dried. Alternatively, an antistatic layer can be formed by using the compound together with a binder such as gelatin, polyvinyl alcohol, cellulose acetate phthalate, cellulose acetate, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polyvinyl phthalate, polymethylmethacrylate, a co-polymer of styrene and maleic acid, cellulose acetate butyrate, cellulose ethylether phthalate, methyl cellulose, ethyl cellulose, polystyrene, cellulose nitrate, a polyurethane resin, a polyamide resin, a phenol resin, a urea resin, a melamine resin, etc. with a suitable amount of the binder being about 0.1 to 2% by weight. The antistatic layer can further contain various additives such as a hardening agent, e.g., formaldehyde, acrolein, chrom alum, etc., a slipping agent, e.g., sodium laurate, sodium stearate, etc., a matting agent, e.g., silica etc., or antihalation dye.

The film support to which the present invention can be applied includes, for example, films of polyolefins such as polyethylene, polystyrene, a co-polymer of styrene and butadiene, cellulose esters such as cellulose triacetate, a polycarbonate, polyvinyl chloride, a polyamide, or polyesters such as polyethylene terephthalate, or baryta paper, synthetic paper-like sheets, or paper are coated with these substances on both sides.

The following Examples specifically illustrate the effects of the present invention. Evaluation of the antistatic ability was made on the basis of the surface resistivity and the occurrence of static marks.

The surface resistivity was measured while a test piece was held by 10 cm long brass electrodes (using stainless steel at the parts contacting the test piece) with a distance of 0.14 cm therebetween, using an insulation meter (Model MM-V-M, Takeda Riken K.K.) to determine a 1-minute value. The measurement was made at 23°C at an RH of 65%.

The static mark generating test was performed by placing an unexposed film on a rubber sheet with the antistatic agentcontaining side facing the rubber sheet, pressing them together by applying a rubber roller on top of the assembly, and then peeling off the film thereby generating static marks on the film. The test was conducted at 23°C at an RH of 30%.

In both tests, the test piece was conditioned under the above conditions for one day.

In order to evaluate the extent of static mark formation, the sample was developed for 5 minutes at 20°C using a developer solution of the following formulation.

Formulation of the Developer Solution		
N-Methyl-p-aminophenol Sulfate	4	g
Sodium Sulfite (anhydrous)	60	g
Hydroquinone	10	g
Sodium Carbonate (monohydrate)	53	g
Potassium Bromide	2.5	g
Water to make	1	liter

The evaluation of static marks was made using grades A to E as shown below.

A: No formation of static marks was observed.

B: Slight occurrence of static marks.

C: Considerable occurrence of static marks.

D: Marked occurrence of static marks.

E: Static marks occurred all over the surface.

EXAMPLE 1

An antistatic solution of the following formulation was coated on one surface of a polyethylene terephthalate film, and on the other surface, an emulsion for indirect roentgenography containing 9% of gelatin and 9% of silver halide was coated.

	Antistatic Solution			
	I		II	
Compound of This Invention	0.010	g	0.017	g
Cellulose Triacetate	0.34	g	0.34	g
Solvent (a 70/8/8/2 mixture of ethylene chloride, methanol, tetrachloroethane, and phenol)	105	g	105	g

The surface resistivity of the back surface of the processed film obtained and the state of static mark formation obtained are shown in Table 1 below.

Table 1

Antistatic Agent	Antistatic Solution	Surface Resistivity	Static Mark Formation
Compound (1)	I	4×10^{11}	A
	II	2×10^{11}	A
Compound (4)	I	6×10^{11}	A – B
	II	4×10^{11}	A
Compound (6)	I	4×10^{11}	A
	II	3×10^{11}	A
Compound (13)	I	8×10^{11}	A – B
	II	4×10^{11}	A
Blank	—	more than 1×10^{16}	E

The use of the compounds in accordance with this invention resulted in a marked decrease in surface resistivity, and a marked inhibition of the formation of static marks. On the other hand, developed static marks occurred all over the surfaces of the untreated films.

EXAMPLE 2

An antistatic solution of the following formulation was coated on one surface of a cellulose triacetate film, and an indirect roentgenographic emulsion was coated on the other surface.

Formulation of the Antistatic Solution		
Compound of This Invention	0.3	g
Methanol	80	ml
Acetone	20	ml

The surface resistivity of the back surface of the processed film obtained and the state of static mark formation obtained are shown in Table 2 below.

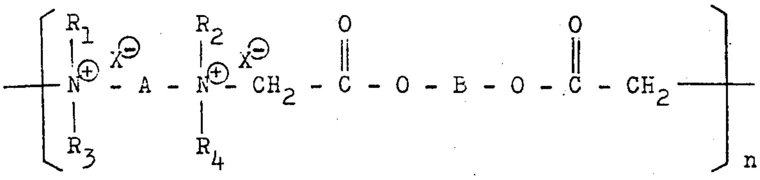
Table 2

Antistatic Solution	Surface Resistivity	Static mark Formation
Compound (1) of This Invention	2×10^{11}	A
Compound (6)	3×10^{11}	A
Compound (13)	1×10^{11}	A
Blank	more than 1×10^{16}	E

Static marks were not formed in the films including the compounds in accordance with this invention, but developed static marks occurred all over the surfaces of the untreated films.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof. What is claimed is:

1. An antistatic photographic material comprising a support having thereon a photographic emulsion layer and a layer containing a compound expressed by the following formula



$$\left[\overset{R_1}{\underset{R_3}{\overset{|}{\underset{|}{N^{\oplus}}}}} X^{\ominus} - A - \overset{R_2}{\underset{R_4}{\overset{|}{\underset{|}{N^{\oplus}}}}} X^{\ominus} - CH_2 - \overset{O}{\overset{\|}{C}} - O - B - O - \overset{O}{\overset{\|}{C}} - CH_2 \right]_n$$

wherein A and B each represent a straight chain or branched chain alkylene group, a xylylene group or a cyclohexylene group, in which the straight chain or branched chain alkylene group may contain a double bond, a triple bond or a $-(CH_2CH_2O)_y-CH_2-CH_2-$ group in the alkylene moiety; R_1, R_2, R_3 and R_4 each represent a lower alkyl group, or R_1 and R_2 and/or R_3 and R_4 may be combined together to form a nitrogen-containing heterocyclic ring; X is an anion; n is an integer of 20 to 50; and y is an integer of 1 to 20.

2. The antistatic photographic material of claim **1**, wherein X is a halogen atom.

3. The antistatic photographic material of claim **1**, wherein said layer is a surface layer and the amount of said compound is 0.01 to 1.0 g per square meter of the surface layer.

4. The antistatic photographic material of claim **3**, wherein the amount of said compound is 0.03 to 0.4 g per square meter of the surface layer.

* * * * *