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ANTISTATIC LAYER FOR PHOTOGRAPHIC MATERIALS

Karl-Otto Meyer, Leverkusen, Richard Schiffmann, Cologne-Flittard, and Wolfgang Himmelmann, Cologne-Stammheim, Germany, assignors to Agfa-Gevaert Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany

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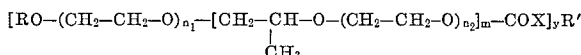
Int. Cl. G03c 1/06, 1/82

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2 Claims

ABSTRACT OF THE DISCLOSURE

Certain polyglycol derivatives are very effective antistatic agents for photographic films carrying gelatin layers. These agents are of the formula:



wherein:

R is an alkyl having 6–18 carbon atoms, a phenyl group including a substituted phenyl group;

X is 0 or an imino group;

R¹ is a y-valent organic group of the phenyl or naphthyl series;

n₁ or n₂ is an integer from 4 to 8;

m is 0 or 1 and

y is 1, 2, or 3.

Great difficulties arise both in the production and in the use of photographic films owing to accumulation of electric charge. These static electric charges may be caused by friction between the film and the rollers or other parts of the apparatus through which the film runs, where contact is made with rough surfaces or as a result of numerous other factors. Static discharges occurring in the film before development are recognizable after the film has been worked up by the presence of irregular stripes or lines, or dark points, which are caused by the spark exposure of the emulsion at these positions. The presence of static charge in the processed film is also undesirable, especially in the case of cinematographic film, since it increases the friction of the film as it runs through the projector.

Electrostatic charging of the film surface can be reduced by adding matting agents to the protective layers to diminish the adhesion between two surfaces of the photographic material which are in contact with each other. The formation of electrostatic charges can also be avoided by the addition of electrically conductive materials to an outermost layer.

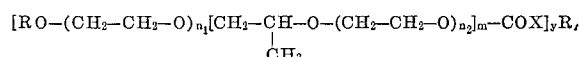
Many of these additives which have a satisfactory antistatic action, are of limited utility since they deleteriously effect the photographic properties.

Thus, quaternary salts cannot be used in photographic materials because they cause fogging. Hygroscopic materials such as glycerol, potassium acetate or lithium chloride cause the layers to adhere to each other and are ineffective at low humidities. High molecular carboxylic or sulfonic acids such as sodium salts of polystyrene sulfonic acid and polyvinylsulfonic acid have a good antistatic effect when applied direct to a hydrophobic layer support, but this effect is greatly reduced when used in gelatin or emulsion layers. Chromium complexes react with gelatin and therefore can only be used under certain conditions.

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It is among the objects of the present invention to provide antistatic agents that are photographically inert and that can be used as additives to photographic protective layers.

We now have found that photographically inert urethanes or esters of hydroxyalkylated fatty alcohols or hydroxyalkylated alkylphenols that are sparingly soluble in water are excellently suitable as antistatic additives for photographic layers preferably gelatin layers. The compounds of the invention are characterized by the following formula:



wherein:

R=alkyl having preferably 6–18 carbon atoms, aryl, preferably phenyl, aralkyl such as benzyl or phenylethyl or cycloalkyl such as cyclohexyl; the above substituents, especially the phenyl groups, may be further substituted in any way desired;

X=a simple chemical bond or a bivalent imino group;

R' is a y-valent organic group of the kind defined under R;

n₁ and n₂ are integers from 4 to 8 inclusive;

m=0 or 1; and

y=1, 2 or 3.

These copolymers (in the case where m=1) are block polymers and not compounds which contain ethylene oxide and propylene oxide in statistical distribution.

The compounds to be used in accordance with the invention are generally highly viscous, syrupy substances. When used for photographic purposes, they are dissolved in a photographically inert solvent, preferably a low molecular weight aliphatic alcohol, and this solution is emulsified into the casting solution of the protective layer. In the final layer the antistatic agents are substantially heterogeneously distributed in the layer in the form of fine particles.

The compounds according to the invention are employed in quantities of 0.03 to 0.20 g., preferably 0.05 to 0.075 per g. of the binding agent. They may be used alone or in combination with surface active substances such as anionic or non-ionic wetting agents or in combination with anti-Newton additives such as polystyrene, polymethacrylic acid esters or urea formaldehyde polymers. The last mentioned additives are also present in the final layer in the form of heterogeneously distributed particles having a size of 1–3 microns. Smooth layers that have an excellent antistatic effect are thereby obtained.

As binding agents for the antistatic layer there can be used the hydrophilic and water-permeable film-forming compounds customarily employed for photographic layers, for example proteins preferably gelatin, cellulose derivatives such as alkyl cellulose for instance hydroxyethyl cellulose or carboxyl methyl cellulose, alginic acid and derivatives thereof, polyvinyl alcohols, polyvinyl pyrrolidone and the like.

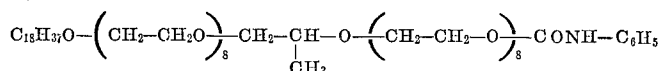
The compounds to be used according to the invention can be used in light-sensitive silver halide emulsion layers, antihalation layers and NC-layers for black-white or color-photographic films. They do not cause fogging, do not accelerate development, do not migrate from the layers or cause sticking of the layers.

The antistatic agents are sparingly soluble in water and are photographically inert. When m=0 (see general formula) they have preferably at the most a total of 8 ethylene oxide units. When the groups R are strongly hydrophobic, the compounds contain preferably more than 8 ethylene oxide units so that they are more readily capable of being emulsified.

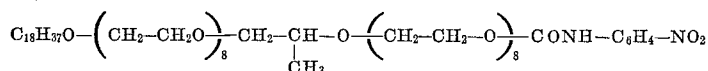
Suitable compounds include those of the following formulae:

neutralizing with hydrochloric acid after removal of the charcoal by filtration under suction. The solvent is re-

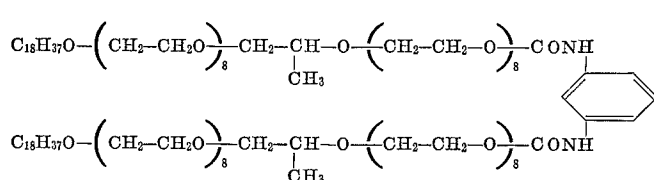
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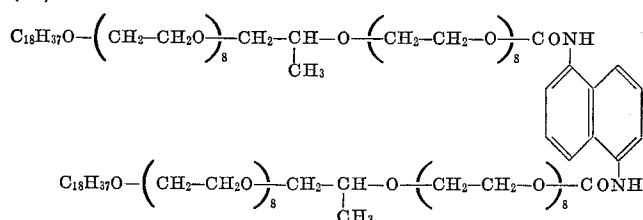
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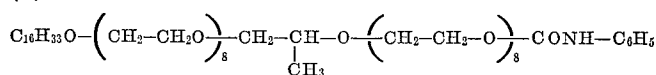
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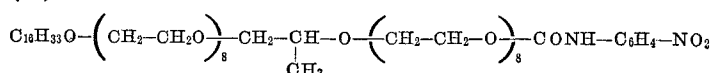
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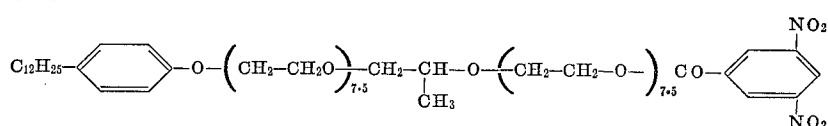
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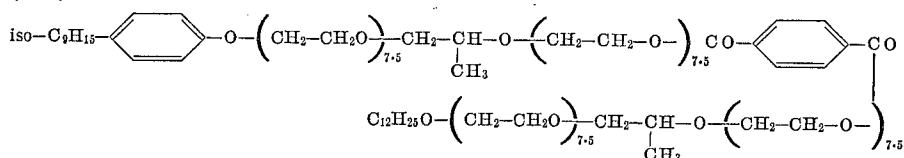
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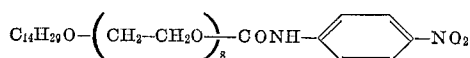
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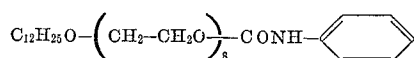
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(IX)



(X)



The compounds to be used according to the invention are prepared by known methods. The preparation of compounds 1 and 7 is described in detail below. The other compounds are prepared in a similar manner.

COMPOUND 1

270 g. of octadecanol and 5 g. of potassium hydroxide are dehydrated at 120° C. and 15 mm. Hg and then reacted with 352 g. of ethylene oxide (8 mols) at temperatures between 160 and 170° C. Directly following this reaction, 58 g. of propylene oxide (1 mol) are incorporated by condensation, and a further 352 g. of ethylene oxide are then reacted. The product is purified by boiling the reaction mixture in 1.5 liters of benzene under reflux with active charcoal for 20 minutes and

moved in a rotary evaporator. The oily, yellow brown product is again filtered at 80 to 90° C.

52.0 g. of hydroxyalkylated octadecanol (as described above) are dissolved in 150 ml. of absolute toluene, and the solution is mixed with a solution of 6.0 g. of phenylisocyanate in 100 ml. of absolute toluene and stirred for 5 hours at 110° C. The reaction mixture is then boiled with 1 ml. of methanol for 5 minutes. After briefly boiling with active charcoal, removing the charcoal by filtration under suction and removing the solvent, a pale brown product is obtained which has a honeylike consistency.

COMPOUND VII

A solution of 9.9 g. of 3,5-dinitrobenzoyl chloride in 150 ml. of benzene is added dropwise to a mixture of 42 g. of n-dodecylphenol which has been hydroxyalkylated in a manner analogous to Compound 1, 20 ml. of benzene and 5 g. of pyridine, and the reaction mixture is stirred at room temperature for 5 hours and at 50° C. for one hour. After cooling, the reaction mixture is

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poured on ice, acidified with 2 N H_2SO_4 , treated with saturated sodium chloride solution, and extracted several times with methylene dichloride. The combined extracts are freed from solvent after drying over K_2CO_3 in a vacuum.

EXAMPLE 1

Samples of a silver iodobromide gelatin emulsion layer on cellulose acetate support are overcoated with protective layers about 1.1 to 1.3μ in thickness which contain different antistatic agents. The casting solution for the protective coatings have the following composition:

1 kg. of gelatin
50 l. of water
3.75 l. of 2% aqueous mucochloric acid as hardener
0.5 l. of 7.5% saponin
0.9 l. of 10% methanolic solution of an antistatic agent.

The 10% methanolic solution of the antistatic agent is emulsified into the casting composition at temperatures between 30 and 40° C. with stirring. The pH of the casting solution which is to form the protective coating is adjusted to 6.5 with sodium hydroxide solution.

The protective coating is applied by usual methods after the emulsion layer has solidified or simultaneously with the application of the emulsion layer by the vacuum air brush process.

The antistatic effect is tested after air conditioning the sample strips for 2 days, the electrostatic charging in volts per cm. (v./cm.) is determined by means of the rotating field strength measuring instrument according to Schwenkhausen. The intensity of charge was measured at 60% relative humidity.

	v./cm. (60% humidity)
Standard (without additive) -----	150
Compound I -----	1
Compound II -----	1
Compound III -----	1
Compound IV -----	1
Compound V -----	2
Compound VI -----	2
Compound VII -----	0
Compound VIII -----	0
Compound IX -----	2
Compound X -----	1

EXAMPLE 2

45 ml. of a 10% methanolic solution of one of the above mentioned antistatic materials is incorporated by emulsification as described in Example 1 into a gelatin solution of the following composition:

1000 ml. of water
110 g. of gelatin
60 ml. of a 10% aqueous solution of fuchsin
18 ml. of a 5% aqueous solution of chrome alum
4 ml. of a 5% aqueous solution of saponin and
30 ml. of ethyl alcohol.

The casting solution is applied onto the rear side of a transparent support of cellulose acetate and dried. The layer serves as a non-curling layer. The other side of the support is coated with a silver halide gelatin emulsion layer.

The antistatic test of the resulting layer are preformed as in Example 1:

	v./cm. (60% humidity)
Standard (without additive) -----	1200
Compound III -----	130
Compound IV -----	140
Compound VI -----	180

EXAMPLE 3

15 ml. of a 10% solution of one of the above mentioned antistatic agents is incorporated by emulsification

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as described in Example 1 into a gelatin solution having the following composition:

1000 ml. of water
30 g. of gelatin
7.5 ml. of a 5% aqueous solution of triacrylic formal
15 ml. of a 5% aqueous solution of saponin.

This solution is applied as protective layer onto the light-sensitive silver halide gelatin emulsion layers of a multi-layered color photographic material and dried.

Antistatic tests of the final layers are performed as described in Example 1:

	v./cm. (60% humidity)
Standard (without additive) -----	100
Compound III -----	15
Compound IV -----	24
Compound VI -----	12

EXAMPLE 4

A photographic material comprising a silver iodobromide gelatin emulsion layer and an uppermost protective layer which does not contain an antistatic agent is treated with 0.01 to 0.25% solutions of the antistatic agents mentioned hereinafter

(a) in water or
(b) in methylene dichloride.

The electrostatic charge of the air conditioned samples is measured at 60% humidity. Comparison measurements are carried out on samples of photographic material which have been treated only with water or methylene dichloride but have otherwise the same composition.

Antistatic tests of the samples

(a) application of antistatic agent from aqueous solution:

	v./cm. (60% humidity)
Without antistatic agent -----	120
Compound V -----	50
Compound X -----	12

(b) application of antistatic agent from methylene dichloride solution:

	v./cm. (60% humidity)
Without antistatic agent -----	20
Compound V -----	0.5
Compound X -----	2

EXAMPLE 5

The following example illustrates the possibility of combining the antistatic agents according to the invention with known antistatic agents. Representatives of two groups of antistatic agents are used, namely:

(a) polystyrene sulfonic acid as representative of high molecular weight compounds which contain carboxyl or sulfone groups, and
(b) various alkali metal salts (with the exception of NaCl) which do not coagulate gelatin.

The antistatic agents are incorporated into a protective gelatin layer which is applied onto a silver iodobromide gelatin emulsion layer according to Example 1. This layer contains, either alone or in combination, as will be seen from the following tables, based on the dry weight of gelatin, 20% by weight of polystyrene sulfonic acid (PSS), 6% by weight of alkali metal salt or 6% by weight of the antistatic agent according to the invention.

After application of the protective layer, the samples are dried, and the antistatic properties are tested after 2 days' air conditioning (60% relative humidity as de-

scribed in Example 1). The results are shown in the following table:

Inventive compounds	Additives PSS	Salts	Electrostatic charge in volt/cm.	Surface resistivity in 10^{10} ohm
Gelatin.....	(¹)	-----	150	8.1
	+	-----	15	2.1
	+	-----	0.5	0.9
Compound III.....	+	Plus KNO ₃	0.5	0.7
	+	Plus Na ₂ SO ₄	0.5	0.9
	+	-----	9	1.5
	+	Plus KNO ₃	3	1.2
	+	Plus Na ₂ SO ₄	4	1.2
	+	-----	3	1.6
Compound IV.....	+	Plus KNO ₃	1	1.4
	+	Plus Na ₂ SO ₄	1	1.4
	+	-----	1.5	1.3
	+	Plus KNO ₃	1	0.9
	+	Plus Na ₂ SO ₄	1	1.2
	+	-----	0.2	2.2
Compound VI.....	+	Plus KNO ₃	0.5	1.5
	+	Plus Na ₂ SO ₄	0.4	1.1
	+	-----	1	2
	+	Plus KNO ₃	2.5	1.5
	+	Plus Na ₂ SO ₄	1	1.5

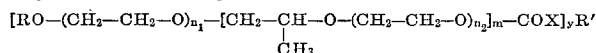
¹ Layer without antistatic additives.

The surface resistivity is determined with a measuring instrument which has two comb electrodes 10 cm. in length arranged parallel to each other at a distance of 2 cm., and the samples which have been adequately air conditioned, are pressed at a constant pressure against these electrodes. The resistivity is registered with a teraohmmeter connected to the instrument.

What is claimed is:

1. In an electrically non-conductive support carrying a photographic gelatin emulsion layer and an effective

amount of an antistatic agent, the improvement according to which such agent has the formula:



wherein

R is an alkyl having 6-18 carbon atoms, a phenyl group including a substituted phenyl group;

X is O or an imino group;

R' is a y-valent organic group of the phenyl or naphthyl series;

n_1 or n_2 is an integer from 4 to 8;

m is 0 or 1 and

y is 1, 2 or 3.

2. The combination of claim 1 wherein the layer contains the antistatic agent in amounts of 0.03 and 0.02 g. per g. of the gelatin in the said layer.

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WILLIAM D. MARTIN, Primary Examiner

M. SOFOCELEOUS, Assistant Examiner

U.S. Cl. X.R.

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