

[54] **PHOTOGRAPHIC MATERIAL WITH
IMPROVED ANTISTATIC PROPERTIES**

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Related U.S. Application Data

[63] Continuation of Ser. No. 252,026, May 10, 1972,
abandoned.

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[58] Field of Search..... **96/87 A**

[56] **References Cited**
UNITED STATES PATENTS

2,373,282	2/1961	Gross	106/308
3,066,851	4/1963	Wagner.....	23/277
3,525,621	8/1970	Miller	96/87 A
3,635,714	1/1972	Oshibuchi et al.....	96/87 A

FOREIGN PATENTS OR APPLICATIONS			
1,009,187	11/1965	United Kingdom.....	96/87 A

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Assistant Examiner—J. P. Brammer
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[57] **ABSTRACT**
Light sensitive photographic material containing silver halide emulsion and auxiliary layers on a support one or more layers thereof contain finely divided silica particles and an orthophosphoric acid in which at least two hydroxyl groups are esterified with monoesterified or monoetherified polyalkylene glycols. The material shows improved antistatic properties.

3 Claims, No Drawings

PHOTOGRAPHIC MATERIAL WITH IMPROVED ANTISTATIC PROPERTIES

This application is a continuation of copending U.S. application Ser. No. 252,026, filed May 10, 1972 and now abandoned, entitled Photographic Material with Improved Antistatic Properties. This invention relates to a process for preventing triboelectric charging occurring in photographic layers which contain gelatin, while maintaining all the other properties necessary for the casting and processing of photographic material.

The way in which photographic layers which have been applied to transparent layer supports, or to paper backed with synthetic resin, respond to contact and friction plays an important role in the production and processing of photographic materials. Static charging and discharging caused by friction and sticking on contact gives rise to accidental exposure of the light sensitive layers and may cause sticking of the finished photographic material when rolled up.

It is known that the antistatic properties of photographic materials can be reduced by the addition of particles of so-called spacer substances which are heterogeneously incorporated in the layer, e.g. particles of polyacrylonitrile, formaldehyde-urea polycondensates or silica of different particle sizes, or by the addition of lubricating substances which increase the sliding property, e.g. stearins, waxes, oil emulsions or silicone emulsions, these substances being either added to the individual photographic layers or applied to the back of the layer support.

When the so-called spacer substances mentioned above are added to a protective layer or to a photographic emulsion, they often cause abrasion when the photographic materials are processed or used in projectors. Lubricant substances may cause undesirable changes in the surface structure when variations in moisture or temperature occur and may thereby interfere with development.

Other known antistatic substances have a deleterious effect on the photographic properties of the light sensitive layers, for example quaternary salts usually give rise to fogging in photographic emulsions. Hygroscopic substances such as glycerol, potassium acetate, sodium chloride or lithium chloride cause the layers to stick or withdraw residual moisture from the emulsion and gelatin layers when the atmospheric humidity is low. Both the fragility and the charging of the layer and layer support are thus increased.

Most of the known higher molecular weight carboxylic or sulphonic acids, e.g. sodium polystyrene sulphonate and sodium polyvinyl sulphonate, have a good antistatic effect when directly applied to a hydrophobic layer support but they often act as a brake to the layers and increase their coefficient of dynamic friction. Their antistatic effect is considerably impaired when they are used in combination with gelatin or photographic silver halide emulsions.

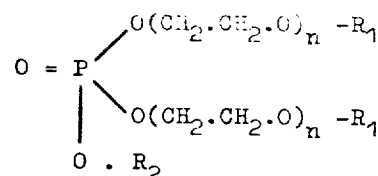
Silica has the desirable effect of loosening the structure of the layers but the effect in reducing the charging of the photographic material is only slight. Large particles of silica may have a deleterious effect and impair the quality and sharpness of the image due to abrasion.

It is an object of this invention to develop photographic materials which have improved antistatic properties.

A photographic material containing at least one silver halide emulsion layer on a support has now been found in which a gelatin layer contains finely divided silica particles and an orthophosphoric acid in which at least two hydroxyl groups are esterified with monoesterified or monoetherified polyalkylene glycols.

Antistatic charging of the photographic layers and the layer support are practically completely suppressed in the material according to the invention. In addition, sliding friction and sticking on contact are greatly reduced. The photographic properties of the layer are not deleteriously affected and the mechanical properties, e.g. the breaking strength are even improved.

The most suitable phosphoric acid esters are those of the following formula:



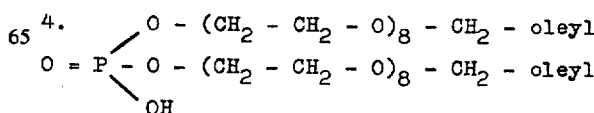
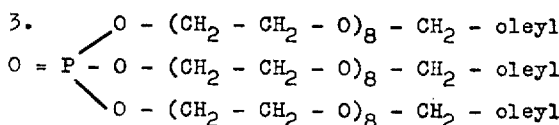
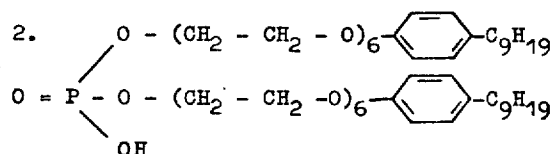
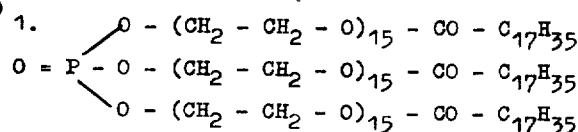
in which

R_1 is (1) an aliphatic radical containing up to 18 carbon atoms, (2) an aralkyl group such as a benzyl group, (3) an aryl radical (especially phenyl radicals) which may be substituted and (4) an acyl radical, in particular acyl radicals which are derived from aliphatic carboxylic acids containing up to 20 carbon atoms;

R_2 is a hydrogen atom or the group $(\text{CH}_2\text{CH}_2\text{O})_n - \text{R}_1$,

n is 4 to 50, preferably 8 to 20.

The following are examples of phosphoric acid esters which are particularly suitable:



Other suitable phosphoric acid esters and their method of preparation have been described, e.g. in British Patent Specification No. 1,009,187.

These compounds are soluble in water and/or CH_3OH .

Silica which has been prepared by a pyrogenic or by a wet method is suitable for use in combination with these phosphoric acid esters. Silica produced by a pyrogenic method is particularly suitable. If silica which has been prepared by a wet method is used, the casting solution for the layers which contain silica are sometimes not sufficiently stable, especially at the pH values of 5 to 7 and especially 6.5 normally required for photographic layers. These casting solutions must then be used as soon as possible after they have been prepared. Pyrogenic silicas do not have this disadvantage.

The silica is added to the antistatic layers in the form of aqueous dispersions or as sols. The concentration may vary within wide limits. It has been found suitable to use dispersions which have a silica content of about 10 to 40% and preferably about 20 to 30%. The particle sizes of the silica should be between 5 and 200 nm and preferably between 10 and 40 nm.

Silica particles which have the properties indicated below are particularly suitable.

Technical data of silica prepared by a pyrogenic method and of a mixed oxide $\text{SiO}_2/\text{Al}_2\text{O}_3$	
Surface according to BET m^2/g	80 ± 30
Size of primary particles	10 to 40 nm, preferably 20 to 30 nm
Loss on ignition (according to DIN 52 911) determined after 2 hours at 1000°C on a substance which has previously been dried at 105°C for 2 hours	<1%
pH (according to DIN 53 200) in a 4% aqueous dispersion	3.6 - 4.2
SiO_2	>98.3%
Al_2O_3	0.3 - 1.3%, preferably 1%
Grit according to Mocker (DIN 53 580)	0.1%

According to a preferred embodiment of the invention, the silica contains a small proportion of aluminium oxide, between 0.1 and 5% and preferably between 0.3 and 1.5%.

The addition of secondary or tertiary esters of orthophosphoric acid and polyethylene glycol to photographic layers is already known per se. The esters are added to the layers as plasticisers and at the same time produce a slight antistatic effect. The addition of silica sols to photographic layers is also already known. In the known processes, the silica was added either as matting agent or to improve the antistatic properties. The effect is relatively slight and is combined with the disadvantages indicated above.

The combination according to the invention of these two components produces an unexpected synergistic effect. A particularly surprising feature is that the surface resistance of the layers or of the layer support is only slightly reduced by the combination according to the invention whilst charging of the layers and the layer support disappears practically completely. This unexpected effect is presumably due to the fact that the capacity of phosphoric acid esters to take up a positive static charge and of silica particles to take up a negative

static charge cancel each other out in the presence of proteins, in particular the presence of gelatin used as binder. Thus, the triboelectric charging of the layers or layer support is prevented or reduced to such a slight extent that the possibility of accidental exposure is eliminated.

Another surprising feature is that when silica is combined with these phosphoric acid esters in accordance with the invention, the addition of silica to gelatin layers no longer has any deleterious effect. Silica normally has a thixotropic action and causes thickening of gelatin solutions to which it is added.

When using the combination according to the invention, the casting solution for the photographic layers undergoes no change in viscosity and the formation of agglomerates, which is particularly troublesome when projecting small size films and television films, is also absent.

The total quantity of silica and phosphoric acid esters used as well as the proportion by weight of these components to each other may vary within wide limits. The optimum quantities, which depend on the desired effect and on the composition of the given photographic layer, can easily be determined by a few simple laboratory tests. It has generally been found sufficient to add silica and phosphoric acid esters to the photographic layers in quantities of 1 to 30% by weight based on the layer forming compound, in particular gelatin. The proportion of the two components to each other may be between 1:10 and 10:1. The exceptionally high antistatic effect of this combination is practically independent of the pH of the layer. Spreading and creeping to adjacent layers, e.g. when storing a photographic material in the form of a roll, does not occur.

The antistatic combination according to the invention of silica and phosphoric acid esters may be added to the photographic layers at any stage of their preparation but preferably after chemical ripening and shortly before casting.

The silica and phosphoric acid esters may be added to any photographic layer, e.g. to silver halide emulsion layers or to gelatin-containing back coating or protective layers. The antistatic compounds may, of course, also be added to several layers.

The layer binding substances used may be proteins, preferably gelatin, if desired mixed with other hydrophilic, water permeable, film forming substances. Starch and starch derivatives, cellulose and cellulose derivatives, alginic acid and derivatives thereof, polyvinyl alcohol, polyvinyl pyrrolidone and the like, for example, may be used as layer binding substances either alone or as mixtures with gelatin.

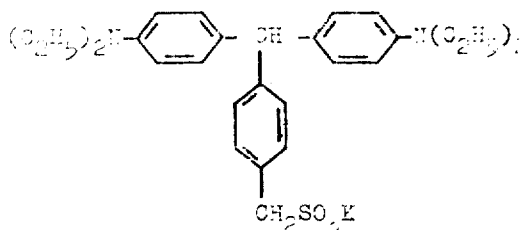
The antistatic effect is measured with a rotary electrostatic field strength measuring instrument of the type FM 300 — NR 1 of Prof. Dr. Ing. F. SCHWENK-HAGEN (Manufacturers: Bergischer Feingerätebau Wuppertal) after 2 days air conditioning of the sample strips. The value measured is the intensity of the charge at 60% relative humidity. The surface resistance is determined with a measuring instrument of Lindenblatt, Elektrotechnik und Elektronik, Berlin-Halensee. This instrument has two parallel comb electrodes 10 cm in length situated 2 cm apart, against which the samples are pressed at a constant pressure after having been air conditioned for a sufficient length of time. The resistances are read off a teraohmmeter connected to the measuring instrument.

EXAMPLE 1

Aqueous solutions of the following composition are applied to sample strips of layer supports of cellulose acetate:

Layer 1a.

1000 ml of water
100 g of gelatin,
100 ml of antihalation dye (7.5% in water in accordance with the formula shown below),
30 ml of saponin (7.5% aqueous solution),
20 ml of formalin (10% aqueous solution),
0.5 ml of phenol

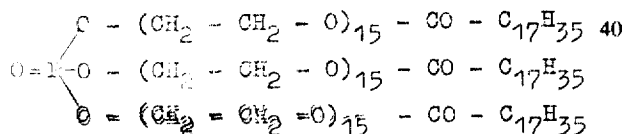


Layer 1b.

the same as (1a) but containing in addition 25 ml of a 28% aqueous silica sol (= 7 g of solid substance/100 g of gelatin) (particle size 25-30 nm)

Layer 1c.

the same as (1a) with the addition of 40 ml of 25% solution of the phosphoric acid ester of the following formula



in water/methanol (1:1) (= 10 g of substance according to the invention per 100 g of gelatin)

Layer 1d.

the same as (1a) with the addition of 65 ml of a mixture of 25 ml of the aqueous silica dispersion described above and 40 ml of the phosphoric acid ester.

The antihalation layer is dried. The thickness of the dried layer is 10 μm . The charge and the surface resistance of the various layers used for comparison were then determined as described above. The results of the electrical measurements are summarised in the table below.

Layer	Charge comparison values in V/cm	Surface resistance in Ohm
1a	+ 135	$3.0 \cdot 10^{10}$
1b	- 95	$2.7 \cdot 10^{10}$
1c	+ 15	$3.0 \cdot 10^{10}$
1d	- 5	$9.3 \cdot 10^9$

EXAMPLE 2

Sample strips of a colour photographic material consisting in the usual way of a layer support carrying a red sensitive silver halide emulsion layer with a cyan coupler, a green sensitive silver halide emulsion layer with a magenta coupler, a yellow filter layer and a blue sensitive layer with a yellow coupler are covered with protective gelatin layers μm in thickness obtained from aqueous solutions of the following composition:

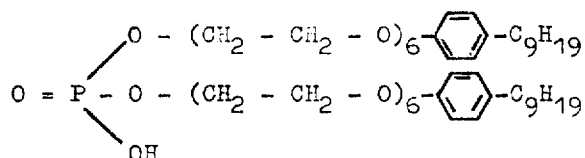
Layer a

1000 ml of water,
20 g of gelatin,
25 ml of 7.5% aqueous solution of saponin,
20 ml of a 5% aqueous solution of basic chromium triacetate,
0.5 ml of a 5% methanolic solution of 1-hydroxy-3-methyl-4-chlorobenzene;

Layer b

Composition the same as (a) with the addition of 25 ml of a 28% aqueous dispersion of silica (particle size about 30 nm), solids content 1.4 g/100 g of gelatin;

Layer c Composition the same as (a) with the addition of 8 ml of a 25% solution of the phosphoric acid ester of the following formula



in water/methanol (1:1) (= 2 g of solid substance/100 g of gelatin);

Layer d

Composition the same as (a) with the addition of 5 ml of the silica dispersion and 8 mol of the phosphoric acid ester solution.

The layer is dried and the electric properties of the layer are determined as described above. The results are summarized in the table below:

Layer	Charge comparison values in V/cm	Surface resistance Ohm	Dynamic sliding ability
a)	+ 130	$3.5 \cdot 10^{10}$	0.30
b)	- 90	$1.6 \cdot 10^{10}$	0.27
c)	+ 15	$3.0 \cdot 10^{10}$	0.20
d)	- 2	$3.7 \cdot 10^9$	0.18

The electric properties of dried samples obtained by applying layers of the above composition to the silver halide gelatin emulsion layer of a black-and-white film are shown in the table below.

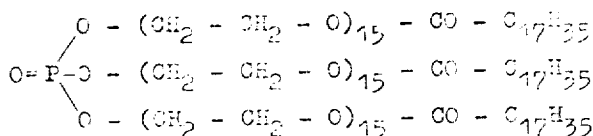
Layer	Charge comparison values in V/cm	Surface resistance Ohm	Dynamic sliding ability
3a	+ 650	$3.0 \cdot 10^{11}$	0.34
3b	+ 330	$1.5 \cdot 10^{10}$	0.28
3c	+ 50	$4.0 \cdot 10^9$	0.22
3d	+ 18	$6.6 \cdot 10^9$	0.20

EXAMPLE 3

a. A light sensitive silver halide emulsion containing 80 g of gelatin per kg of casting solution is cast on a cellulose acetate support and dried. The thickness of the dried layer is 7 μ .

b. The cast layer is covered with a protective gelatin layer of the following composition:

- 1000 ml of water,
20 g of gelatin,
40 ml of a 7.5% aqueous solution of saponin,
10 ml of a 10% aqueous solution of formalin,
5 ml of a 28% dispersion of silica (pyrogenic),
6.7 ml of a phosphoric acid ester (25% dissolved in
1:1 methanol and water) of the following formula:



The thickness of the protective layer when dry is 1.5 μ .

The charge uptake capacity of air conditioned strips is determined by the test method described above. The following values were determined:

A. After charging the sample 3 times with the rotating brush of an electrostatic field strength measuring instrument:

Strips 3(a) (emulsion layer without protective layer)
340 V/cm

Strips of 3(b) (emulsion with protective layer according to the invention) -17 V/cm

B. After charging the samples 27 times:

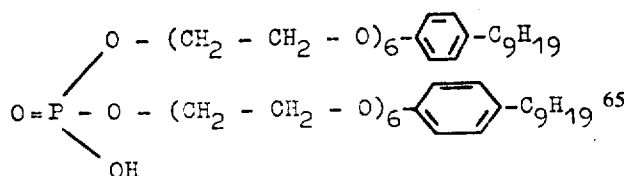
Strips (a) 880 V/cm

Strips (b) — 6 V/cm

EXAMPLE 4

a. 40 ml of a 7.5% aqueous solution of saponin and 20 ml of formalin (10% in water) are added to 1 litre of a panchromatically sensitized silver halide emulsion which contains 80 g of gelatin per litre of emulsion when ready for casting. This solution is cast on a triacetate foil and dried. The thickness after drying is 10 μ .

b. 56 ml of a 25% phosphoric acid compound (dissolved in $-\text{CH}_3\text{OH}/\text{H}_2\text{O}$ 1:1) of the following formula:



are added to 1 litre of the above casting solution.

c. 70 ml of a 28% silica dispersion prepared pyrogenically (containing 1% of Al_2O_3) are added to 1 litre of the casting solution described under 4(a).

d. 70 ml of a silica sol (from SiO_2 prepared by an aqueous method) are added to 1 litre of the casting solution described under 4(a).

e. A combination of
56 ml of the phosphoric acid ester described under
4(b) and

70 ml of the silica sol (as under 4(d) is added to 1 litre of the casting solution described under 4(a).

f. A combination of
56 ml of the phosphoric acid ester described under
3(b) and

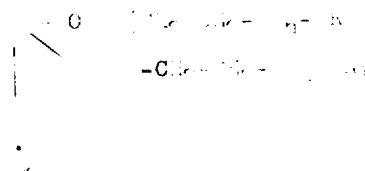
70 ml of the silica dispersion described under 3(c) which has been prepared pyrogenically is added to 1 litre of the casting solution described under 4(a). The results are summarised in the table below

		Charge comparison emulsion side	values in V/cm reverse side	surface emulsion side	resistance in Ohm reverse side
Strips	4a	800	1800	$1.4 \cdot 10^{10}$	$2.5 \cdot 10^{12}$
	4b	50	1200	$2.5 \cdot 10^9$	$3.0 \cdot 10^{12}$
	4c	70	1500	$1.0 \cdot 10^{10}$	$3.0 \cdot 10^{13}$
	4d	80	1200	$7.2 \cdot 10^9$	$2.5 \cdot 10^{12}$
	4e	—40	1200	$1.2 \cdot 10^9$	$3.5 \cdot 10^{12}$
	4f	-20	800	$1.5 \cdot 10^9$	$3.0 \cdot 10^{12}$

No substrate was applied to the back.

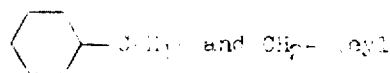
We claim:

1. A light sensitive photographic material having improved antistatic properties containing at least one silver halide gelatin emulsion layer and a layer containing a binder and silica obtained by pyrogenic method and having a BET value of between 50 and 110 m²/g and in said silica-containing layer an orthophosphoric acid ester of the following formula:



in which

R₁ × an aliphatic group with up to 18 carbon atoms,


$$R_2 = H \text{ or } (CH_2CH_2O)_n - R_1 \text{ and } n = 4-15, 15,$$

and in which layer the total weight of phosphoric acid ester and silica is 1 to 33.5% of the weight of layer binder of the photographic layer and the proportion of phosphoric acid ester to silica is between 1:10 and 10:1.

2. Photographic material according to claim 1, characterised in that the silica contains 0.3 to 1.5% by weight of aluminium oxide.

3. Photographic material according to claim 1, characterised in that the silica has a particle size of between 10 and 40 nm.

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