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[54] PHOTOGRAPHIC MATERIALS WITH  
ANTISTATIC LAYERS

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[51] Int. Cl..... **G03c 1/82**  
[58] Field of Search..... **96/87 A, 114.2**

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## [57] ABSTRACT

The antistatic properties of photographic materials can be improved by applying an antistatic layer containing as antistatic agents a mixture of polymers, or a graft polymer, containing sulfo as well as carboxyl groups.

**9 Claims, No Drawings**

# PHOTOGRAPHIC MATERIALS WITH ANTISTATIC LAYERS

The present invention relates to photographic elements comprising a film or paper support having at least one improved antistatic layer.

Because of the accumulation of electric charges on photographic films, serious difficulties arise both in their production and in their use. These static electric charges may be caused, e.g., by friction of the film against the rollers or against other parts of the apparatus through which the film runs, or by contact with rough surfaces. Static discharges cause light-sensitive film to be exposed and irregular stripes, lines or dark patches, therefore appear after photographic processing. The accumulation of static charges on processed films, in particular on those used for cinematography, is also undesirable because such charges increase the friction when the film runs through the gate or other parts of the projector.

Electrostatic charging of the surfaces of the film can be reduced by adding matting agents to the protective layers on the film; these matting agents reduce the bond between two films placed in contact. Once a charge has been produced, it can be removed by electrically conductive additives. The two charge combatting techniques may be combined.

According to another charge combatting technique a conductive or hygroscopic material is usually applied to the surface of the film in order to increase its electrical conductivity. Many of the substances which are effective in this respect, however, are not photographically inert and, therefore, they deleteriously affect the photographic properties.

Thus, for example, quaternary salts in most cases cannot be used in photographic materials because they cause fogging. Hygroscopic substances such as glycerol, potassium acetate or LiCl cause the layers to stick and are ineffective at low atmospheric humidity. Higher molecular weight carboxylic acids or sulfonic acids, e.g., polystyrene sulfonic acid sodium and polyvinyl sulfonic acid sodium, have a good antistatic effect when applied directly to a hydrophobic layer support, but this effect is greatly reduced if the substances are applied in gelatine layers or emulsion layers. Chromium complexes react with gelatine and, therefore, can only be used under certain conditions.

Many compounds which have a good antistatic action alter the casting properties of casting solutions when added to gelatine solutions, with the result that the layers produced have irregular surfaces.

It is among the object of the invention to provide antistatic agents which are photographically inert and which can be used alone or mixed with gelatine.

We now have found a photographic material having at least one silver halide emulsion layer which has an antistatic layer containing, as an antistatic agent, the following substances in the form of a mixture or of a graft polymer:

- I. A polymer having a molecular weight of at least 10,000 of olefinically unsaturated monomers having sulfo groups, and
- II. A polymer having a molecular weight of at least 10,000 of monomers at least 50 mol percent of which contain carboxyl groups that are either in the free or in the neutralised form.

The mixture of polymers containing carboxyl groups and sulfonic acid groups can be prepared quite simply by mixing the two polymers in the required proportions. Preferred, however, are graft polymers which are produced to at least some extent by polymerizing the monomers of one polymer component in the presence of the other polymer. One advantageous method of procedure consists in producing the carboxyl-containing polymers directly in the aqueous solution of a polymer which contains sulfonic acid groups preferably by radical polymerisation.

The proportion by weight of polymer which contains carboxyl groups to polymer which contains sulfonic acid groups may vary within wide limits. Proportions by weight of 1:10 to 10:1 are generally sufficient. Mixtures in a proportion by weight of between 1:3 and 3:1 have been found to be especially advantageous. The polymers may be used in the form of dispersions or emulsions or in the form of their solutions in suitable solvents, especially in water or methanol. They may be partly or completely neutralised. The pH should preferably be between 4 and 8.5.

The carboxyl-containing polymers preferably used, either directly or in the form of their salts, are water-soluble homopolymers and copolymers based on itaconic, maleic, fumaric or methacrylic acid or especially those based on acrylic acid, the homopolymers being preferred. If copolymers are used, the comonomers are preferably hydrophilic monomers such as short-chain vinyl esters, e.g., vinyl acetate, or derivatives of acrylic or methacrylic acid such as amides or short-chained esters of alcohols having up to five carbon atoms particularly those having hydrophilic groups such as esters which contain hydroxyl groups, e.g., hydroxypropylmethacrylate, or allyl compounds such as trimethylolpropane monoalkyl ether. Other comonomers are, of course, also suitable provided they are present in such small quantities that the copolymer remains water soluble in the form of its salt. Such monomers are olefins such as ethylene or propylene, styrene, vinyl chloride, longer chained acrylic acid esters such as butyl acrylate, decylmethacrylate, acrylonitrile etc.

The carboxyl-containing copolymers, which are preferably water-soluble, or the preferred homopolymers should have molecular weights above 10,000 preferably between 50,000 and 3,000,000 and more particular between 50,000 and 1,000,000. Copolymers of higher molecular weights may also be used but these give rise to certain technical difficulties because of the high viscosity of their solutions.

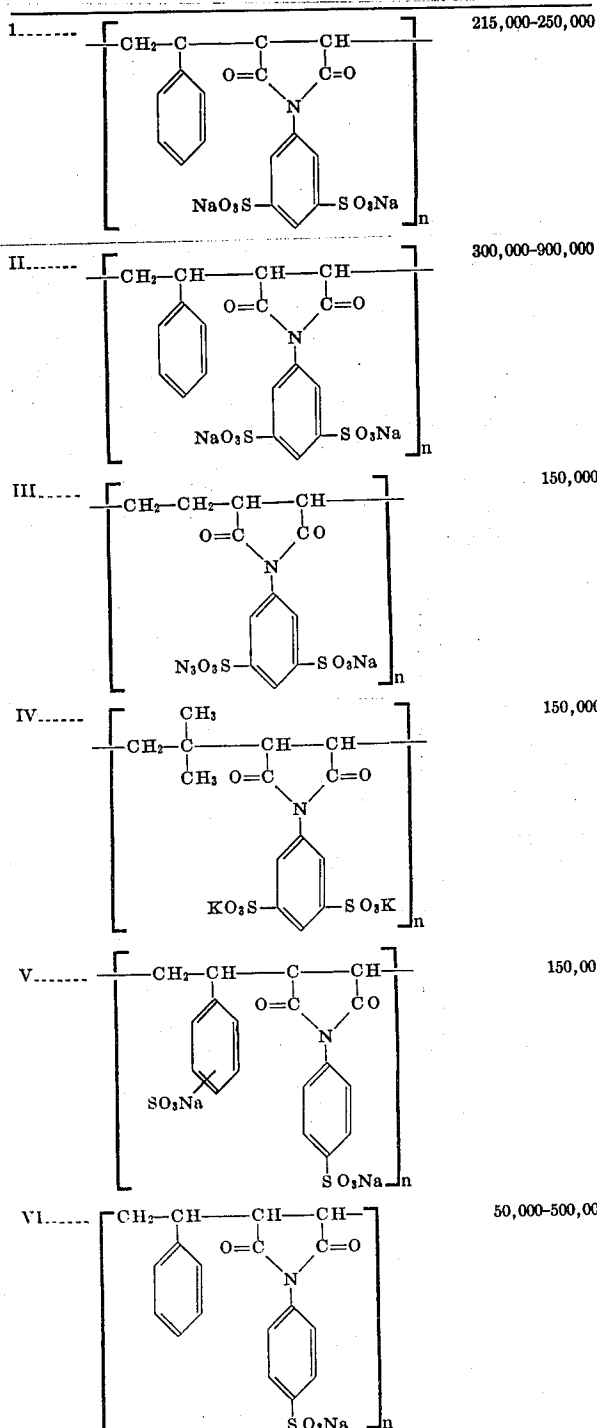
Suitable polymers containing sulfo groups are for example polystyrenesulfonic acid, polyvinylsulfonic acid, poly-N-acryloyl-taurin or the corresponding methacryloyl product, poly-N-acryloyldimethyltaurine or the corresponding methacryloyl polymer, sulfonated polyphenylether or sulfonated rubber. Preferred are polystyrenesulfonic acids having a sulfo content of between 15 and 75 percent by weight preferably 20 - 45 percent by weight more particular between 30 and 44 percent by weight.

Preferred are also copolymers which consist to an extent of 40 to 60 mols percent of units of sulfosubstituted N-phenylmaleic imides and which have a molecular weight of between 50,000 and 70,000. The following are examples of comonomers suitable for these copolymers: Polymerisable olefinically unsaturated aliphatic compounds containing up to five carbon atoms,

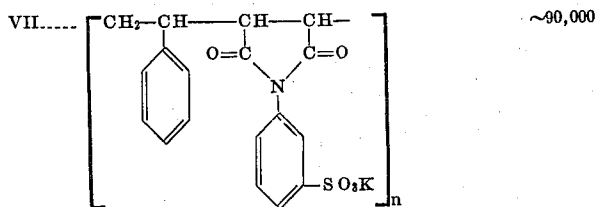
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e.g., ethylene, propylene, butylene, 2-methyl-pentene-1 or isoprene; vinyl alcohol, vinyl esters with aliphatic carboxylic acids containing up to five carbon atoms, e.g., vinyl acetate, vinyl propionate or vinylbutyrate, vinyl ethers in which the ether component is aliphatic and contains up to five carbon atoms, e.g., vinylisobutyl ether; styrene or substituted styrenes, e.g., styrenes which contain sulfo groups. Copolymers of ethylene, isobutylene and/or styrene with sulfosubstituted N-phenylmaleic imides are especially suitable.

A few especially suitable polymers containing sulfo groups are represented below in the form of their idealised formulae and with their average molecular weight:



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The above polymers may be obtained by various methods known per se, especially by reacting copolymers of maleic anhydride with suitable aromatic aminosulphonic acids or their alkali metal salts in aqueous or non-aqueous media at temperatures above 120°C. Water is eliminated in this process and the maleic acid imide ring is formed. The polymers may also be prepared by the sulphonation of copolymers of N-phenylmaleic imide, which itself may be obtained either by the copolymerisation of N-phenylmaleic imide or subsequent reaction of maleic anhydride copolymers with aniline in a reaction involving imidisation.

The preparation of a few polymers is described below by way of example. The parts indicated are parts by weight.

#### POLYMER I

600 parts of NaOH and 4,500 parts of the monopotassium salt of aniline-3,4-disulphonic acid are dissolved in 17,000 parts of water. 3,000 parts of a copolymer of maleic anhydride and styrene which has an approximately alternating structure and which has a viscosity of  $\eta = 0.56$  determined in dimethylformamide at 25°C (molecular weight approximately 100,000) are then added and the reaction mixture is heated in an autoclave at 175°C for 10 hours, a clear solution of Polymer I being formed.

#### POLYMER II

The same method is employed as for polymer I but a copolymer of maleic anhydride and styrene having an approximately alternating structure and a viscosity of  $\eta = 1.5$  (molecular weight approximately 2,500,000) is used.

#### POLYMER III

300 parts of the monopotassium salt of aniline-3,5-disulphonic acid and 40 parts of NaOH are dissolved in 900 parts of water, and 130 parts of a copolymer of ethylene and maleic anhydride which has an alternating structure and an  $\eta$  value of 0.91 (molecular weight approximately 50,000) are added. The reaction mixture is then heated to 170°C for 10 hours and a clear solution of Polymer III is obtained.

#### POLYMER IV

300 parts of the monopotassium salt of aniline-3,5-disulphonic acid and 40 parts of NaOH are dissolved in 1,500 parts of water. 152 parts of a copolymer of isobutylene and maleic anhydride which is approximately alternating in structure and has an  $\eta$  value of 0.7 (molecular weight approximately 65,000) are then added and the reaction mixture is heated to 175°C for 10 hours, a clear solution of Polymer IV being obtained.

#### POLYMER V

10 parts of anhydrous liquid  $\text{SO}_3$  are dissolved in 300

parts by volume of anhydrous  $\text{SO}_2$  at  $-60^\circ\text{C}$ . 20.2 parts of alternating styrene/maleic anhydride copolymer are then introduced with stirring. Stirring is continued for 8 hours at approximately  $-50^\circ\text{C}$  and the reaction mixture is then left to evaporate. The resulting polymer, which is sulphonated in the aromatic nucleus, is then dissolved in 140 parts of water with 8 parts of NaOH and 17.4 parts of sulphanilic acid and heated to  $175^\circ\text{C}$  for 10 hours, during which time imidisation is completed. A clear solution of polymer V is obtained.

#### POLYMER VI

80 parts of NaOH and 346 parts of sulphanilic acid are dissolved in 3,300 parts of water. 400 parts of an equimolar copolymer of styrene and maleic anhydride,  $\eta$  value 0.62, are stirred into this solution and the reaction mixture is heated in an autoclave at  $170^\circ\text{C}$  for 10 hours. A clear, approximately 20 percent solution of the polymeric imide is obtained.

#### POLYMER VII

The same procedure is employed as for Polymer VI, but instead of sulphanilic acid, the corresponding metasulphonic acid is used.

The polymers are preferably completely imidised. In principle, however, the corresponding polymers containing only a slight amount of maleic acid or maleic anhydride units or the half amide are also suitable.

The occurrence of such saponification products cannot always be excluded with certainty even when the method described above of preparation in an aqueous medium is employed, and the above formulae are, therefore, only to be regarded as approximate and are not always strictly applicable for the whole polymer molecule.

#### POLYMER VIII

A mixture of 100 parts of a 10 percent aqueous solution of the sodium salt of polystyrene sulfonic acid, 10 parts of acrylic or methacrylic acid, 0.1 parts of potassium persulfate and 0.05 parts of sodiumpyrosulfite are stirred in a nitrogen atmosphere for 10 hours at  $30^\circ\text{C}$  and for 1 hour at  $50^\circ\text{C}$ . A clear aqueous polymer solution with a solid content of about 16.5 percent by weight is obtained which, as desired, can be neutralized by addition of aqueous sodium hydroxide. The above solution can be added directly to the casting solution for the antistatic layer.

In analogous manner other sulfonated polymers can be used for producing graft polymers with acrylic or methacrylic acid.

The preparation of the antistatic mixtures of polymers containing carboxyl groups and polymers containing sulfonic acid groups used according to the invention will now be described by way of example.

Mixture 1: polyacrylic acid (molecular weight approximately 90,000) is dissolved in a 15 percent aqueous solution of polymer I at  $65^\circ\text{C}$  in such an amount that the resulting mixture has a solids content of 30 percent after neutralisation with NaOH to pH 6.5

Mixture 2: The same as mixture 1 but instead of polymer I, polymer VI (molecular weight 150,000) is used.

Mixture 3: The same as mixture 1 except that instead of polyacrylic acid, a copolymer of 90 parts of methacrylic acid and 10 parts of oxypropyl methacrylate (molecular weight approximately 100,000) is used.

Mixture 4: 7,500 parts of a 15 percent aqueous solution of polymer VI (molecular weight approximately 80,000) are stirred up with 1,275 parts of acrylic acid at  $40^\circ\text{C}$ . 6 parts of potassium persulphate and 3 parts of sodium pyrosulphite are then added. The polymerisation temperature is maintained at a maximum of  $50^\circ\text{C}$ . After about 15 hours, polymerisation is completed and the material is ready for use after it has been neutralised to a pH of 6.5 with 30 percent NaOH. The solids content is 30 percent.

Mixture 5: The same as mixture 4 except that a polymer VI having a molecular weight of about 160,000 is used in this case.

Mixture 6: The same as mixture 4 except that 640 parts of acrylic acid are used. The solids content after adjustment to pH 6.5 is about 22 percent.

The polymers or polymer mixtures used as antistatic agents according to the invention may be clear or cloudy solutions or dispersions. They are photographically inert so that the light sensitive layers are in no way adversely affected.

With the aid of these polymers, smooth, non-sticky layers can easily be cast by adding the polymers to gelatine solutions or to the casting solutions for the silver halide gelatine emulsions. The antistatic action is very high, as will be seen from the examples below.

The polymers are worked up in the form of aqueous solutions having a solids content of up to about 15 percent by weight and preferably 2 to 4 percent so that layers having a thickness of 1.5 to  $2\ \mu$  when dry are obtained. The conductivity depends on the thickness of the layer. With the thickness indicated, sufficient conductivity is ensured. The compounds mentioned above have layer forming properties. They may be used alone or with the addition of water permeable protective colloids such as gelatine. The amount of layer colloids present may be up to 10 times the quantity of antistatic agent but is preferably not more than 20 percent (based on the dry weights).

Surface active substances such as anionic or non-ionic wetting agents or anti-Newton matting additives may be added as auxiliary agents to the layers according to the invention, e.g., particles measuring 1 to  $5\ \mu$  of polystyrene, polymethacrylic acid esters or urea formaldehyde condensates or  $\text{SiO}_2$ . Smooth layers which have an excellent antistatic action are obtained in this way.

The layers according to the invention are applied in the usual manner as uppermost protective layers to the set of layers and may be used for black and white as well as for colour photographic materials. In principle, however, these antistatic layers could be arranged anywhere, both on the emulsion side and on the rear surface or they may be applied directly to the support or in the emulsion itself.

The antistatic action is tested after 2 days air conditioning of sample strips, using rotating electrostatic field strength measuring instruments of the type FM 300 - NR I of Prof. Dr. Ing. F. Schwenckhagen (Manufacturers: Bergischer Feingeratebau, Wuppertal). The extent of charging at 60 percent relative humidity is measured. The surface resistance is determined with a measuring instrument of Lindenblatt, Elektrotechnik und Elektronik Berlin-Halensee. The instrument has two comb electrodes 10 cm in length which are parallel to each other 2 cm apart, and the samples, which have been sufficiently air conditioned, are pressed against

these electrodes at a constant pressure. The resistances are read off a Tera-Ohmmeter connected to the instrument.

#### EXAMPLE 1

In a protective layer for photographic materials containing 20 g of gelatine per litre of water, half the gelatine was replaced successively by antistatic agents 1 to 6. As casting aid 12 ml of a 5 percent aqueous solution of saponine as wetting agent were added per litre of solution. The thickness of the dried layer was 1.5  $\mu$ . Measurements were carried out as indicated above.

	Surface resistance in Ohms	Chargeability in V . cm <sup>-1</sup>
Pure gelatine layer	4.4 . 10 <sup>10</sup>	60
Protective layer with mixture 1	1.2 . 10 <sup>8</sup>	10
Protective layer with mixture 2	9.2 . 10 <sup>7</sup>	1
Protective layer with mixture 3	2.4 . 10 <sup>8</sup>	8
Protective layer with mixture 4	1.3 . 10 <sup>8</sup>	5
Protective layer with mixture 5	3.4 . 10 <sup>7</sup>	1
Protective layer with mixture 6	4.8 . 10 <sup>8</sup>	1

#### EXAMPLE 2

20 g of antistatic agents 1 to 6 were added per litre of emulsion to a panchromatic photographic silver halide emulsion containing about 60 g of gelatine and 35 g of AgBr for black and white photography. The emulsion was applied onto a support of cellulose triacetate. Measurements were:

	Surface resistance in Ohms	Chargeability in V . cm <sup>-1</sup>
Emulsion alone	1.4 . 10 <sup>11</sup>	30
with mixture 1	6.4 . 10 <sup>8</sup>	5
with mixture 2	5.6 . 10 <sup>7</sup>	-3
with mixture 3	1.2 . 10 <sup>9</sup>	2
with mixture 4	7.6 . 10 <sup>8</sup>	4
with mixture 5	1.4 . 10 <sup>9</sup>	-5
with mixture 6	3.8 . 10 <sup>8</sup>	-1

#### EXAMPLE 3

To the silver halide emulsion of Example 2 were added the following polymers (based on the gelatine content of the emulsion):

- 30 percent by weight of a graft polymer of one part acrylic acid on one part of polystyrene sulfonic acid,
  - 30 percent by weight of a mixture of polystyrene sulfonic acid and polyacrylic acid (1:1),
  - 30 percent by weight of polystyrene sulfonic acid.
- The silver halide emulsion is applied onto a support of polyethyleneterephthalat.

The results of the measurements of the surface resistance are shown in the following table:

	surface resistance in Ohms 60 % rel. humidity
control without additive	2.2 . 10 <sup>10</sup>
a)	2.0 . 10 <sup>8</sup>
b)	1.5 . 10 <sup>8</sup>
c)	3.0 . 10 <sup>9</sup>

#### EXAMPLE 4

Onto a photographic silver halide gelatine emulsion layer on a baryta coated paper support were applied the following antistatic layers from a 2 percent aqueous solution of the antistatic agent. The dried layers had a thickness of 1.5 microns:

- 85 percent by weight of a polymerization product produced by polymerizing one part acrylic acid in the presence of one part polystyrene sulfonic acid (39.7 percent by weight sulfo groups) 15 percent by weight gelatine;

- a layer of the polymerization product of (a) having the same thickness.

The results of the measurements of the surface resistance at different humidity are shown in the following table:

	surface resistance in Ohms 60 % rel. humidity	30 %
control without additive	2.2 . 10 <sup>10</sup>	1.2 . 10 <sup>12</sup>
a)	4.0 . 10 <sup>9</sup>	5.5 . 10 <sup>11</sup>
b)	2.2 . 10 <sup>7</sup>	1.1 . 10 <sup>9</sup>

We claim:

- In a photographic material including a support, at least one silver halide emulsion layer on the support and an antistatic layer, the improvement according to which the antistatic layer contains a mixture or a graft polymer of a polymer having a molecular weight of at least 10,000 of olefinically unsaturated monomers having sulfo substitution, with a water-soluble polymer having a molecular weight of at least 10,000 of monomers at least 50 mol percent of which are substituted by carboxyl groups that are free or neutralized, the proportion by weight of the two polymers being from 1:10 to 10:1.

- The photographic material of claim 1, wherein the polymer containing sulfo groups is a polystyrene sulfonic acid containing between 15 and 75 percent by weight sulfo groups.

- The photographic material of claim 1 wherein the polymer containing sulfo groups is a copolymer containing at least 40 percent by weight of units of sulfosubstituted N-phenylmaleicimides.

- The photographic material of claim 1, wherein the antistatic layer also contains gelatine.

- The photographic material of claim 1 wherein the polymer containing sulfo groups is a copolymer selected from the group consisting of ethylene and isobu-

tylene and sulfosubstituted N-phenylmaleicimide units.

6. The photographic material of claim 1, wherein the polymer containing carboxyl groups is polymethacrylic acid or polyacrylic acid.

7. The photographic material of claim 1, wherein the polymer containing sulfo groups is a copolymer consisting essentially of styrene and N-4-sulfophenylmaleic

imide units.

8. The photographic material of claim 1, wherein the polymers are grafted together.

9. The photographic material of claim 8, wherein the graft is the result of polymerizing the carboxylsubstituted monomers in the presence of the sulfosubstituted polymer.

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