

[72] **Inventors** **Karl-Otto Meyer**
Leverkusen;
Wulf Von Bonin, Leverkusen; Wolfgang
Himmelmann, Cologne-Stammheim; Julius
Geiger, Leverkusen; Werner Wagenknecht,
Cologne-Suelz, all of Germany

[21] **Appl. No.** **881,599**
 [22] **Filed** **Dec. 2, 1969**
 [45] **Patented** **Oct. 26, 1971**
 [73] **Assignee** **Agfa-Gevaert Aktiengesellschaft**
Leverkusen, Germany

[32] **Priority** **Dec. 20, 1968**
 [33] **Germany**
 [31] **P 18 15 944.9**

[51] **Int. Cl.**..... **G03c 1/78**
 [50] **Field of Search**..... **96/94,**
114.2, 114, 67

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

2,279,410	4/1942	Nadeau	96/87
3,039,870	6/1962	Laakso	96/87

Primary Examiner—Norman G. Torchin
Assistant Examiner—J. R. Hightower
Attorney—Connolly and Hutz

[54] **ANTISTATIC LAYERS CONTAINING POLYMERS**
OF SULFO-SUBSTITUTED N-PHENYL MALEIC
IMIDES
4 Claims, No Drawings

[52] **U.S. Cl.**..... **96/67,**
96/87, 96/114.2

ABSTRACT: A photographic material with improved anti-static properties. The material contains an outermost anti-static layer of a polymer containing N-phenyl maleic imides units.

ANTISTATIC LAYERS CONTAINING POLYMERS OF SULFO-SUBSTITUTED N-PHENYL MALEIC IMIDES

The present invention relates to photographic materials which have improved antistatic protective layers.

Great difficulties arise both in the production and in the use of photographic films because of the accumulation of electrostatic charges. These electrostatic charges may be caused, e.g., by friction of the film against the rollers or other parts of the apparatus through which the film runs, or by contact with rough surfaces. The film is exposed by static discharges. Irregular strips, lines or dark spots are, therefore found after photographic processing. The occurrence of static charges on processed films, particularly those intended for cinematographic purposes, is also undesirable because this increases the friction as the film runs through the projector.

The electrostatic charge on the surfaces of films can be reduced by adding matting agents to the protective layers so as to reduce the adhesion between two films when they are in contact. Once a charge has accumulated, it can be removed by means of electrically conductive additives which are applied to the surface of the film so as to increase the electrical conductivity of the film. Many substances which are effective for this purpose, however, are not photographically inert with the result that the photographic properties of the film are impaired.

Thus quaternary salts usually cannot be used in photographic materials because they cause fogging. Hygroscopic substances such as glycerol, potassium acetate or LiCl cause sticking of the layers and are ineffective when the humidity is low. When higher molecular weight carboxylic or sulfonic acids such as the sodium salt of polystyrene sulfonic acid and the sodium salt of polyvinyl sulfonic acid are applied directly to a hydrophobic layer support, they show a good antistatic effect but this effect is greatly reduced when the compounds are used in gelatine and are, therefore, only of limited utility.

Many compounds which show a good antistatic effect alter the casting properties of casting solutions when added to gelatine solutions, with the result that irregular layer surfaces are formed.

It is among the objects of the invention to provide antistatic agents which are photographically inert and which can be used either alone or in admixture with gelatine.

We now have found photographic material having at least one silver halide emulsion layer and a topmost antistatic layer which contains as an antistatic agent, a polymer of olefinically unsaturated monomers having a molecular weight of at least 15,000, the polymer containing at least 40 mol. percent of sulfo-substituted N-phenyl maleic imides in polymerized form.

Copolymers which consist of between 40 to 60 mole percent of units of sulfo-substituted N-phenyl maleic imides are preferred.

Polymers which have a molecular weight of between 50,000 and 500,000 are particularly useful.

The following are examples of suitable comonomers which may be used for the preparation of the copolymers which are to be used according to the invention: polymerizable olefinically unsaturated aliphatic compounds which have up to 5 carbon atoms, e.g., ethylene, propylene, butylene or isoprene; vinyl alcohol, vinyl esters with aliphatic carboxylic acids which have up to 5 carbon atoms, e.g., vinyl acetate, vinyl propionate or vinyl butyrate, and vinyl ethers in which the ether component is aliphatic and contains up to 5 carbon atoms, e.g., vinyl isobutyl ether; and styrene or substituted styrenes, e.g., styrenes which contain sulfo groups. Copolymers of ethylene, isobutylene and/or styrene with sulfo-substituted N-phenyl maleic imides are particularly advantageous.

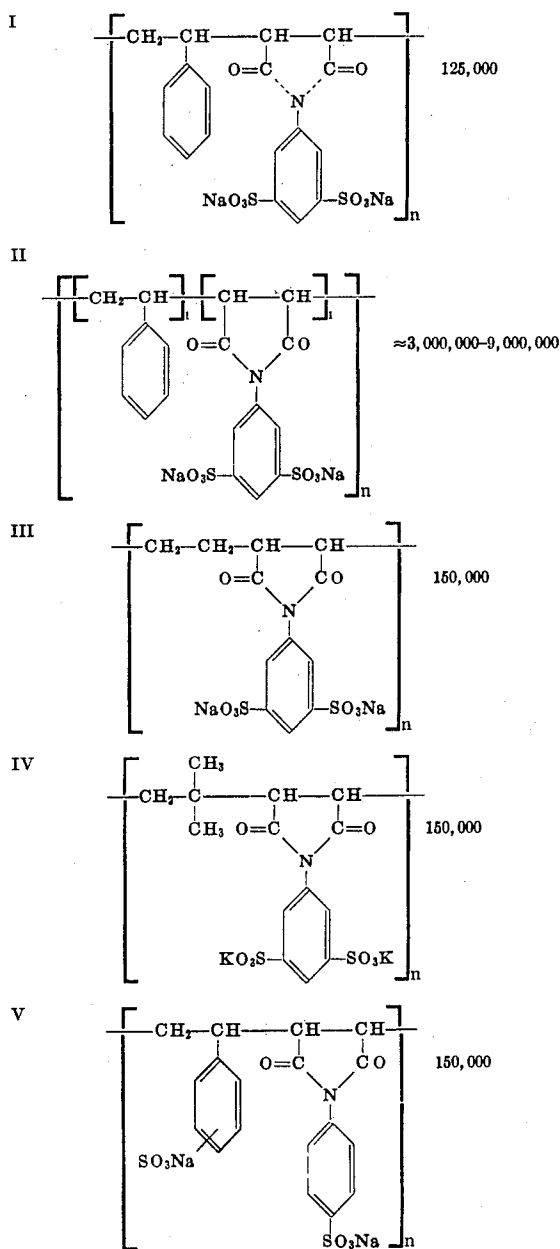
The sulfo groups are generally present in neutralized form as alkali metal salts in particular as sodium or potassium salts.

The excellent properties of the antistatic layers according to the invention are due to the sulfo substituted N-phenyl maleic imide units. The aromatic character of the imide group is particularly important for this purpose. Copolymers which contain an aliphatic group instead of the phenyl ring in a corresponding position are much inferior to N-phenyl maleic imide copolymers in their antistatic effect in their suitability for photographic layers.

The polymers to be used according to the invention also have an excellent ability to form films. They are eminently compatible with other binders and are photographically unreactive so that the light-sensitive layers are in no way adversely affected.

Smooth, nonsticky layers can easily be case with the polymers. The antistatic action is exceptionally high, as will be shown in the examples. As a general rule, the more sulfo groups in the polymer, especially in the phenyl ring of the N-phenyl maleic imide units, the greater is the antistatic action.

Some particularly suitable compounds and their formulas and their average molecular weights are indicated below:



The compounds to be used according to the invention are obtainable by employing various methods of the prior art, particularly by reaction maleic acid anhydride copolymers with suitable aromatic amino sulfonic acids or their alkali metal salts in aqueous or nonaqueous media at temperatures above 120° C., the maleic acid imide ring being formed with elimination of water. The polymers can also be obtained by sulfonating copolymers of N-phenyl maleic imide which can be obtained either by the copolymerization of N-phenyl maleic imide or subsequent to the reaction of maleic anhydride copolymers with aniline in a reaction involving imidation.

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

Polymer I

600 parts of NaOH and 4,500 parts of the monopotassium salt of aniline-3,5-disulfonic acid are dissolved in 17,000 parts H₂O. 3,000 parts of a maleic anhydride styrene copolymer which has an approximately alternating structure and which has an *n* value of 0.56 (molecular weight approximately 100,000) determined in dimethyl formamide at 25° C. 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 obtained.

Polymer II

The procedure is the same as for polymer I but a maleic anhydride styrene copolymer which has an *n* value of 1.5 (molecular weight approximately 2,500,000) and which has an approximately alternating structure is used.

Polymer III

300 parts of the monopotassium salt of aniline-3,5disulfonic acid and 40 parts of NaOH are dissolved in 900 parts of water, and to this are added 130 parts of an ethylene maleic anhydride copolymer of value 0.91 (molecular weight approximately 50,000) which has an alternating structure. The reaction mixture is then heated at 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-disulfonic acid and 40 parts of NaOH are dissolved in 1,500 parts of water. 152 parts of an isobutylene maleic anhydride copolymer of *n* value 0.7 (molecular weight approximately 65,000) which has an approximately alternating structure are then added and the reaction mixture is heated at 175° C. for 10 hours, a clear solution of polymer IV being obtained.

Polymer V

10 parts of anhydrous liquid SO₃ are dissolved in 300 parts by volume of anhydrous SO₂ at -60° C. 20.2 parts of styrene maleic anhydride copolymer of alternating structure are then introduced with vigorous stirring. Stirring is continued for 8 hours at about -50° C. and the reaction mixture is then left to evaporate. The resulting polymer which is sulfonated in the aromatic nucleus is then dissolved with 8 parts of NaOH and 17.4 parts of sulfanilic acid in 140 parts of water and heated at 175° C. for 10 hours, during which time imidation takes place. A clear solution of polymer V is obtained.

The polymers to be used according to the invention are preferably completely imidized. In principle, however, the corresponding polymers which still contain a small amount of maleic acid or maleic anhydride units or the half-amide are also suitable.

The formation of such saponification products cannot always be prevented absolutely even in the above described preparation in an aqueous medium, so that the above formula is to be regarded as only an approximate formula and in some cases may not apply strictly to the whole of the polymer molecule.

The polymers are worked up in the form of aqueous solutions with a polymer content of up to 15 percent by weight, preferably 2 to 4 percent, to yield layers which have a thickness when dry of 1.5 to 2 μm. The conductivity depends on the thickness of the layer. Sufficient conductivity is ensured with the thickness mentioned above. The above-mentioned compounds have layer forming properties and dry to form a clear, transparent layer. They can be used alone or with

the addition of water permeable protective colloids such as gelatine. The amount of protective colloids may be up to 50 percent of the quantity of antistatic agent but is preferably not more than 20 percent (based on the dry weights). Layers which contain substantially only the maleic imide polymers, however, are particularly preferable.

Surface active substances such as anionic or nonionogenic wetting agents or anti-Newton additives such as particles of size 1 to 5 μm. of polystyrene, polymethacrylic acid esters or urea formaldehyde polycondensates may be added to the layers according to the invention as auxiliary agents. Smooth layers with an excellent antistatic action are obtained in this way.

The layers according to the invention are arranged in the usual manner, with protective layers uppermost on the other layers and can be used for black-white and color photographic materials. In principle, these antistatic layers could be arranged in any position, both on the front side and on the rear side of the support.

The antistatic action is tested after two days air-conditioning of the sample strip. The test is carried out with a rotating electrostatic field strength measuring instrument of the type FM 300-NR I by Prof. Dr. Ing. F. Schwenckhagen (manufacturers: Bergischer Feingeratebau, Wuppertal). The concentration of charge at 60 percent relative atmospheric humidity was measured. The surface resistance is determined in a measuring instrument of Firma Lindenblatt, Elektrotechnik und Elektronik, Berlin-Halensee. The instrument has two comb electrodes 10 cm. in length which are situated parallel to each other at a distance of 2 cm. apart. When the samples have been sufficiently air-conditioned they are pressed at a constant pressure against these electrodes. The resistances are read off a Terraohmometer connected to the instrument.

EXAMPLE I

A silver iodobromide gelatine emulsion layer on a cellulose acetate support is coated with a protective layer about 1.5 to 2 μm in thickness. The casting solution for this protective layer has the following composition: 1 liter of water, 20 g. of a maleic imide polymer (see following table) and 10 ml. of 7.5 percent aqueous solution of saponin as wetting agent.

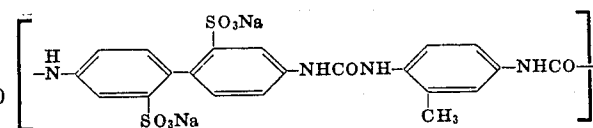
The pH of the casting solution is adjusted to 6.5 with sodium hydroxide solution. The casting solution can be sprayed or applied by any of the usual casting processes at 20° C.

After drying, a smooth layer is obtained which has no fogging, strips, bubbles, patches which are difficult to wet, cloudiness or similar faults, and which lies quite flat.

The results of the antistatic measurements are shown in the following table.

Additive	Chargeability at 60% r.h. humidity 30% (v./cm.)	Surface resistance at 60% rel.	
		(ohm)	(ohm)
none	300	5.2·10 ¹⁰	6.4·10 ¹²
Polymer II 30		5.2·10 ⁷	2.9·10 ⁸
Polymer III	1	5.1·10 ⁸	7.6·10 ⁷
Polymer IV	2	1.8·10 ⁷	5.0·10 ⁷
Polymer V		1.8·10 ⁸	6.0·10 ⁸

A prior art antistatic compound (a polyurea sulfonic acid) containing units of the following formula



shows under the same conditions a surface resistance at 60 percent (relative humidity) of 9,6·10⁸Ω and at 30 percent rel. hum. of 2,5·10⁹Ω.

The photographic material containing the layers according to the invention does not "flash" on processing whereas the comparison material can only be processed at high atmospheric moistures. The photographic properties are not affected.

EXAMPLE 2

Thirty grams of compound I are dissolved in 1,000 ml. of cold distilled water with stirring, using a paddle stirrer. The pH is adjusted to between 6.0 to 7.0 with 1 N sodium hydroxide solution. This antistatic casting solution is applied to a silver chloride emulsion layer after the addition of 24 ml. of 7.5 percent aqueous saponin solution. The layer thickness is 0.5, 1.0 or 2.0 μ .

Results of Measurements

Additive	Surface Resistance (Ω)	Layer Thickness (μ)
none	10^{11}	
Polymer I	$6 \cdot 10^9$	0.5
	$3 \cdot 10^8$	1.0
	$< 10^8$	2.0

These antistatic layers do not only substantially reduce the surface resistance but also prevent the films from sticking.

EXAMPLE 3

A silver iodobromide gelatine emulsion layer on a cellulose acetate support is coated with a protective layer about 1.5 to 2 μ in thickness. The casting solution for this protective layer has the following composition: 1 liter of water, 16 g. of polymer I, 4 g. of gelatine and 10 ml. of a 7.5 percent aqueous solution of saponin.

The pH of the casting solution is adjusted to 6.5 with sodium hydroxide solution. The casting solution can be applied to a layer support at 20° C. in the usual manner.

The following measurement are obtained after drying and air conditioning at 60 percent relative humidity:

	Surface Resistance (Ω)	Layer Thickness (μ)

Table - Continued

Comparison sample	$8 \cdot 10^{10}$	
80% Polymer I+20% gelatine	$2 \cdot 10^8$	1.5

EXAMPLE 4

A silver iodobromide gelatine emulsion layer on a cellulose acetate support is coated with a protective layer of about 1.5 to 2 μ in thickness. The casting solution for this protective layer has the following composition: 1 liter of water, 18 g. of polymer I, 2 g. of polyvinyl alcohol and 10 ml. of 7.5 percent saponin.

The pH of the casting solution is adjusted 6.5 with sodium hydroxide solution.

The following measurements are obtained after the film material has been dried and conditioned at 60 percent relative humidity:

	Surface Resistance (Ω)	Layer Thickness (μ)
Comparison Sample	$8 \cdot 10^{10}$	
Polymer I + 10% polyvinyl alcohol	$5 \cdot 10^7$	1.5

We claim:

1. A photographic material for use in photographic films, said material including a support, at least one silver halide emulsion layer on the support, an outer layer on the emulsion layer, the outer layer containing a polymer of olefinically unsaturated monomers having a molecular weight of at least 15,000 and containing at least 40 mol percent of a sulfo-substituted N-phenyl maleic imide in polymerized form.
2. The photographic material as claimed in claim 1 wherein the said polymer has a molecular weight of between 50,000 and 500,000.
3. The photographic material as claimed in claim 1 wherein the copolymer contains not more than 60 mol percent of units of styrene, sulfosubstituted styrene, ethylene or isobutylene.
4. A photographic material according to claim 1, characterized in that the polymer contains 40 to 60 mol percent of units of a sulfosubstituted N-phenyl maleic imide.

* * * * *

50

55

60

65

70

75

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,615,531

Dated October 26, 1971

Inventor(s) Karl-Otto Meyer et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

- Column 2, line 16, "case" should read -- cast -- .
- Column 3, line 58, period between "imidized" and "In".
- Column 4, line 31, should read -- a distance of 1 cm. -- .
- Column 4, line 34, "Terraohmeter" should read -- Tera-ohmmeter --
- Column 4, the table should read --

Additive	Chargeability at 60% rel. h. (v/cm)	Surface resistance at	
		60% rel. h. (ohm/10cm ²)	30% rel. h. (ohm/10cm ²)
none	300	5.2.10 ¹⁰	6.4.10 ¹²
Polymer II	30	5.3.10 ⁷	2.9.10 ⁸
Polymer III	1	5.1.10 ⁶	7.6.10 ⁷
Polymer IV	2	1.8.10 ⁷	5.0.10 ⁷
Polymer V	-	1.8.10 ⁶	6.0.10 ⁸

Signed and sealed this 29th day of August 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

L