(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 534 006 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **91202473.4**

(22) Date of filing: **24.09.91**

(51) Int. Cl.5: **G03C 1/89**, G03C 1/38

(43) Date of publication of application:
31.03.93 Bulletin 93/13

(84) Designated Contracting States:
BE DE FR GB

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(54) **A photographic light-sensitive material having antistatic properties with good storage stability.**

(57) A photographic light-sensitive material is coated with an antistatic layer comprising an antistatic agent, a polymeric thickener and a fluorinated compound having at least one oxyethylene unit in its molecular structure to improve the preservation of the properties of said antistatic layer after storage of said material for a long time.

EP 0 534 006 A1

1. FIELD OF THE INVENTION

The invention is related to a light-sensitive silver halide photographic material with an anti static layer.

2. BACKGROUND OF THE INVENTION

It is known that a photographic film coated with hydrophilic colloid layers at one or two sides of the undercoat, e.g. a polyester undercoat, has a low conductivity due to the electric-insulating properties and becomes electrostatically charged by friction with dielectric materials and/or contact with electrostatically chargeable transport means, e.g. rollers. The charging occurs particularly easily in a relatively dry atmospheric environment, and especially with rapidly moving mechanical transport systems, the electrostatical charge is accumulated. Said accumulated electrostatical charge may cause various problems due to the fact that it cannot be discharged gradually. As a consequence e.g. partially exposing the photosensitive silver halide emulsion layers of the photographic material after an abrupt discharge may occur before development. This partial exposure results in the formation of dot-like or branch-like or feather-like spots after development of the photographic material.

In praxis the photographic material is subjected to frictional contact with other elements during manufacturing, e.g. during a coating or cutting stage, and during use, e.g. during image-processing. Especially in the reeling-up or unreeling of dry photographic film in a camera high friction may build up, resulting in electrostatic charges that may attract dust or cause sparking. In unprocessed photographic silver halide emulsion materials sparking causes undesirable exposure marks and degrades the image quality. Furthermore these disturbing phenomena cannot be confirmed prior to development. As this phenomenon is very irreproducible difficulties arise for the quality control department to evaluate said photographic material.

In order to reduce electrostatic charging of a photographic material comprising a hydrophobic resin undercoat layer or support and at least one hydrophilic colloid layer on at least one side of said support without impairing its transparency it is known to apply coatings which are formed of or incorporate ionic compounds such as antistatic high molecular weight watersoluble polymeric compounds having ionic groups at frequent intervals in the polymer chain [ref. e.g. Photographic Emulsion Chemistry, by G.F. Duffin, - The Focal Press - London (1966) - Focal Press Limited, p. 168, US-P 4,301,240].

Especially preferred antistatic compositions have been described in US-P 4,610,955. These compositions comprise a hydrophilic binder, a surface active polymer having polymerized oxyalkylene monomers and an inorganic salt of organic tetrafluoroborates,perfluoroalkylcarboxylates,hexafluorophosphates and perfluoroalkyl carboxylates, said fluorinated surfactants leading to a good coating quality of the hydrophylic layers.

To minimize the electrostatic charge properties of photographic materials, especially the tribo-electrical charging causing electrostatical discharges and mechanical faults by transporting, it has been proposed according to EP 0319951 A1 to use in the hydrophilic colloid layer a combination of three surfactants viz. an anionic fluorinated surfactant, a nonionic oxyalkyl compound and a nonionic oxyalkyl compound containing fluorine atoms. Besides a low surface resistance is desirable.

Nevertheless a remaining problem is the preservation of the antistatic properties during storage of the photographic material for a long time after manufacturing, especially when said storage takes place in severe circumstances as e.g. at high temperature and low humidity.

A solution for the preservation problem of the antistatic properties may be offered by the coating of a thicker antistress layer with an increased amount of antistatic agents. These increased amounts give rise to an inadmissable contamination or sludge formation in the processing solutions and a thicker hydrophilic layer may retard the processing and drying velocity.

3. OBJECTS AND SUMMARY OF THE INVENTION.

Therefore it is an object of the invention to provide a photographic material having preserved antistatic characteristics after storage of said photographic material for a long time between manufacturing and processing, even in severe atmospheric conditions.

Another object of the invention is the minimization of the coated amount of antistatic agent and coating additives to reduce the contamination of the processing solutions.

It has been found that the objects can be attained by a photographic silver halide material comprising a support and on one or both sides thereof at least one silver halide emulsion layer and a gelatin antistress layer thereover characterised in that on said antistress layer(s) a substantially gelatin free surface coating is

present containing a polyoxyalkylene antistatic agent and a fluorinated compound with one or more oxyethylene group(s) in its molecular structure.

4. DETAILED DESCRIPTION OF THE INVENTION

According to a preferred embodiment for improving the preservation of antistatic properties the antistatic surface coating is applied by spraying a gelatin free aqueous composition containing the antistatic agent and the oxyethylene fluorinated compound onto the antistress layer(s) or by applying such aqueous composition additionally containing a polymeric non-gelatin thickening agent by known coating techniques such as slide-hopper or curtain coating, preferably together with the antistress coating composition.

The fluorinated compund with oxyethylene groups may be represented by the formula

R_F-A-X (I)

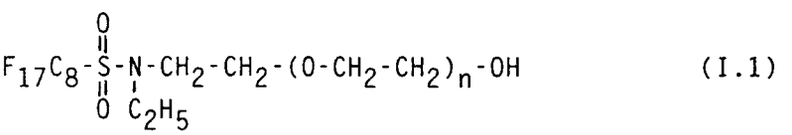
wherein:

R_F stands for a partly or wholly fluorinated hydrocarbon chain comprising at least 3 fluorine atoms,

A stands for a chemical bond, a bivalent hydrocarbon group including a bivalent hydrocarbon group interrupted by one or more hetero atoms, or the group -COO, -CON(R)-, -SO_2N(R)- or SO_2N(R)CO wherein R is hydrogen or alkyl comprising from 1 to 5 C-atoms,

X stands for a hydrophilic oxyalkylene group containing one or more oxyethylene groups.

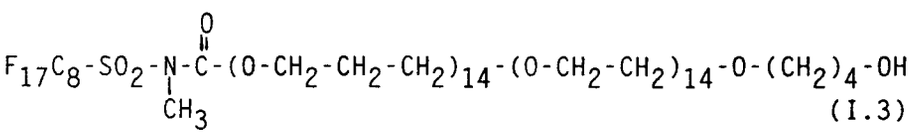
Representative examples of said compounds are given in formulae (I.1) to (1.5) :



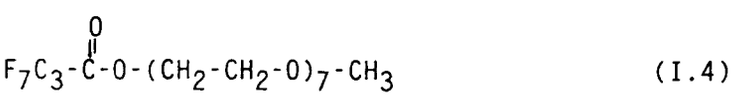
(I.1)

n being equivalent to a value of about 8.

$F_{17}C_8$-(CH_2-CH_2-O)$_6$-H (I.2)



(I.3)



(I.4)

(I.5)

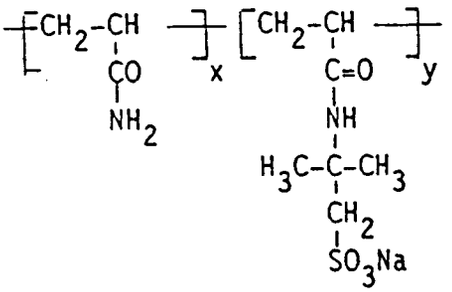
Any of the generally known polyethylene oxide polymers is useful as antistatic agent; a preferred antistatic agent is a polyethylene oxide compound corresponding to formula (II)

R-O-(CH_2CH_2O)$_n$-H (II)

wherein n is an integer of at least 4 preferably between 8 and 30 and R represents a long chain alkyl or

alkylaryl group having at least 10 C-atoms as e.g. oleyl.

Any thickening agent may be used so as to regulate the viscosity of the solution used for slide-hopper or curtain coating provided that they do not particularly affect the photographic characteristics of the silver halide light-sensitive photographic material. Preferred thickening agents include aqueous polymers such as polystyrene sulphonic acid, sulphuric acid esters, polysaccharides, polymers having a sulphonic acid group, a carboxylic acid group or a phosphoric acid group, polyacrylamide, polymethacrylic acid or its salt, copolymers from acrylamide and methacrylic acid and salts derived thereof, copolymers from 2-acrylamido-2-methyl-propansulphonic acid, polyvinyl alcohol, alginate, xanthane, carraghenan and the like. Polymeric thickeners well-known from the literature resulting in thickening of the coating solution may be used independently or in combination. Patents concerning thickening agents are U.S. Patent No. 3.167.410, Belgian Patent No. 558.143, JP OPI Nos. 53-18687 and 58-36768 and DE 3,836,945. As a preferred polymeric thickener use can be made of the product characterized by formula (III)



(III)

with x/y varying from 5/95 to 95/5.

As referred to hereinbefore the antistatic layer can not only be coated from a solution by means of well-known techniques as slide hopper coating or curtain coating but can also be spray-coated. Beyond advantages offered by the spray-coating technique as there is the possibility to perform a coating without hydrophilic colloid binder a much more important advantage consists in the application of a strongly reduced coated amount of polyoxyethylene compound antistatic agent of 10 mg/m^2 where normal amounts being coated from solutions are about 40 mg/m^2. As a consequence the thickness of the aftercoat layer is reduced to 0.5 to 1.0 μm, whereas with curtain coating or slide hopper coating techniques the thickness varies between 7 and 10 μm.

To achieve the described objective additives can be atomized using ultrasonic vibration and the atomized additives can be sprayed onto the coating previously applied on the continuously moving support as has been described in US-P 4,218,533.

The application of a thin layer of antistatic agent to the top surface of a photographic material, particularly during the manufacturing of such photographic material after the drying thereof has been described in EP Application 91/200202 providing a coating station for the performance of the process, requiring limited maintenance and having a high degree of reliability. Extremely thin outermost layers without or with a minimum amount of binder can be forced to a semi-dry or completely dry protective layer.

A common support of a photographic silver halide emulsion material is a hydrophobic resin support.

Hydrophobic resin supports are well known to those skilled in the art and are made e.g. of polyester, polystyrene, polyvinyl chloride, polycarbonate, preference being given to polyethylene terephthalate.

The hydrophobic resin support may be provided with one or more subbing layers known to those skilled in the art for adhering thereto a hydrophilic colloid layer. Suitable subbing layers for polyethylene terephthalate supports are described e.g. in US-P 3,397,988, 3,649,336, 4,123,278 and 4,478,907.

For the composition of silver halide emulsion layers whereto said antistatic layer may be applied reference is made e.g. to Research Disclosure 17,643 of December 1978, and Research Disclosure 307,105 of November 1989.

Photographic silver halide emulsion materials containing an antistatic layer according to the present invention may be of any type known to those skilled in the art. For example, the antistatic layer is useful in continuous tone or halftone photography, microphotography and radiography, in black-and-white as well as colour photographic materials.

In a particular embodiment of the present invention the antistatic coating is applied to a radiographic material that is provided at both sides of the support with a silver halide emulsion layer and an anti stress layer coated thereover. The radiographic material preferably has on both sides of the film support silver

halide emulsion coatings that are split into two distinctive emulsion layers having silver halide crystals of different average grain size one of which is a high speed emulsion layer and the other is a low speed emulsion layer; the high speed emulsion layer being situated at a larger distance from the support than the low speed emulsion layer. This way the sensitometric curve can be fine-tuned, giving the perfect profile for the specific application. Moreover even without using a separate anticrossoverlayer this layer arrangement reduces crossover, especially in the critical low density area. Otherwise crossover preventing filter layers should be used which leave a colour stain upon processing, especially upon rapid processing in less than 60 seconds.

By using a recording material having an antistatic layer according to the present invention the problems caused by static charges prior to processing can be avoided or substantially reduced. Such means for example that the formation of static charges by contact of a silver halide emulsion layer side with the rear side of the recording material or caused by friction with substances such as rubber and hydrophobic polymeric binder, e.g. the binder constituent of phosphor screens used as X-ray intensifying screens, can be markedly reduced by employing the present antistatic layer. The building up of static charges and subsequent dust attraction and/or sparking, e.g. during loading of films in cassettes, e.g. X-ray cassettes, or in cameras, or during the taking of a sequence of pictures as occurs in automatic cameras or film projectors is prevented.

The example hereinafter set forth is directed to the use of an antistatic layer in combination with a polyethylene terephthalate resin support but other resin bases, e.g. made of polystyrene, polyvinyl chloride, cellulose ester such as cellulose triacetate, or polyethylene either or not treated by corona-discharge and/or subbed with (a) subbing layer(s) for improving the adherence of hydrophilic colloid layers will obtain a strong reduction in surface resistance when coated with the herein described antistatic layer,

The following examples illustrate the present invention without however limiting it thereto.

EXAMPLE

In praxis an x-ray photographic material was coated with an antistatic layer as an outermost layer on top of the protective layer covering the silver halide emulsion layer. In the composition of said outermost layer the presence of the three products, described by the formulae (I.1), (II) with n = 10 and R = oleyl, and (III) with x/y = 24/76 are present: the three products were added to an aqueous solution containing up to 10% of ethyl alcohol with respect to the finished solution, ready for coating. Said three products were present in an amount of 0.75 g/l, 6.0 g/l and 6.5 g/l respectively and coated in an amount of 6.0 mg/m^2, 40.0 mg/m^2 and 52.0 mg/m^2 respectively. The amount of ethyl alcohol was evaporated during the coating and drying procedure of the antistatic layer. In this example use was made of the slide hopper coating technique for simultaneous application of the emulsion layer, the antistress layer and the antistatic coating.

In a comparative coating, the fluorinated compound represented by formula (I.1) was replaced by an ammoniumperfluorocarbonate compound represented by the formula $F_{15}C_7COONH_4$ having no polyoxyethylene chain in its molecular structure. An amount of 3.0 mg/m^2 of this compound was coated, being about the equivalent molar amount of the comparative compound according to this invention.

As an objective evaluation of the antistatic properties the surface resistivity has been measured.

The surface resistivity measurement takes place before subjecting said layers to an aqueous processing treatment for photo-exposed photographic silver halide emulsion layer materials. In Table 1 a comparison has also been made between the surface resistivity of a freshly prepared photographic material and said material after storing for 36 hours in a conditioned atmosphere of 57 °C and 34% RH (relative humidity).

The surface resistance, taken as a representive parameter to characterize the antistatic properties of the material, is expressed in ohm/square (ohm/sq.) and is measured by a test proceeding as follows :

- two conductive copper poles having a length of 10 cm parallel to each other were placed at a distance of 1 cm onto the surface to be tested and the resistance built up between said electrodes is measured with a precision ohm-meter. By multiplying the thus determined ohm value with the factor 10 the surface resistance value expressed as ohm/square (ohm/sq) is obtained.

Table 1

Lateral Surface Resistivity for an x-ray photographic film coated with an outermost antistatic layer.		
Coating composition	Lateral Surface Resistivity (in ohm/sq x10^{10})	
	Freshly coated	Conditioned (36 h 57 ° C/34%RH)
Invention	63	81
Comparative example	75	4300

The difference in effectiveness of both products, respectively according to the invention and used as comparative example, with respect to the antistatic character after severe storage conditions, is quite clear: a remarkable improvement in the preservation of the antistatic characteristics has been reached.

Claims

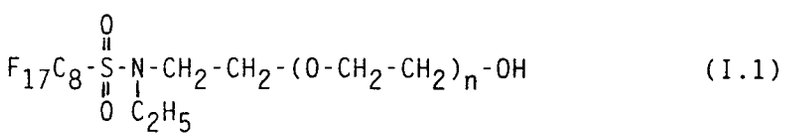
1. A photographic silver halide material comprising a support and on one or both sides thereof at least one silver halide emulsion layer and a gelatin antistress layer thereover characterised in that on said antistress layer(s) a substantially gelatin free surface coating is present containing a polyoxyalkylene antistatic agent and a fluorinated compound with one or more oxyethylene group(s) in its molecular structure.

2. A photographic material according to claim 1, wherein said fluorinated compound has a structure corresponding to formula (I):

R_F-A-X (I)

wherein:
R_F stands for a partly or wholly fluorinated hydrocarbon chain comprising at least 3 fluorine atoms,
A stands for a chemical bond, a bivalent hydrocarbon group including a bivalent hydrocarbon group interrupted by one or more hetero atoms, or the group -COO, - CON(R)-, -SO_2N(R)- or SO_2N(R)CO wherein R is hydrogen or alkyl comprising from 1 to 5 C-atoms,
X stands for a hydrophilic oxyalkylene group containing one or more oxyethylene groups.

3. A photographic material according to claim 2, wherein said fluorinated compound has a structure corresponding to formula (I.1)



(I.1)

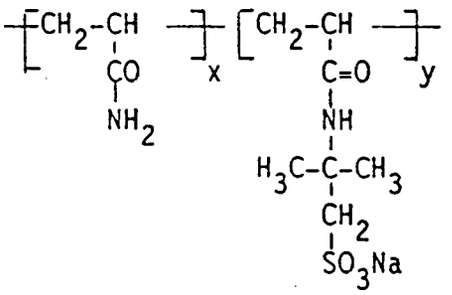
n being equivalent to a value of about 8.

4. A photographic material according to claim 1, wherein said antistatic agent has a structure corresponding to formula (II):

R-O-(CH_2CH_2O)$_n$-H (II)

wherein n is an integer of at least 4, and R
represents a long chain alkyl or alkylaryl group having at least 10 C-atoms.

5. A photographic material according to claim 1 , wherein said surface coating comprises a polymeric thickener having a structure corresponding to formula (III):



(III)

wherein x/y varies from 5/95 to 95/5.

6. A photographic material according to claim 5, wherein said polymeric thickener is present in an amount of 20 to 150 mg/m^2.

7. A photographic material according to any of claims 1 to 6, wherein said fluorinated compound is coated in the antistatic layer(s) in an amount of 2 to 20 mg/m^2.

8. A photographic material according to any of claims 1 to 7, wherein said antistatic agent is present in an amount of 10 to 150 mg/m^2.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 20 2473

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 300 259 (MINNESOTA MINING AND MANUFACTURING CO.) * abstract * * page 12, line 28 - line 34 *	1	G03C1/89 G03C1/38
X	WORLD PATENTS INDEX LATEST Section PQ, Week 8910, Derwent Publications Ltd., London, GB; Class P83, AN 89-072264 & JP-A-1 024 245 (ORIENTAL PHOTO IND KK) 26 January 1989 * abstract *	1,2	
A	EP-A-0 370 226 (AGFA-GEVAERT AKTIENGESELLSCHAFT) * page 32, line 37 - page 33, line 35 * * page 36, line 21 - line 36 *	1,5,6	
A	EP-A-0 242 853 (KONISHIROKU PHOTO-INDUSTRY CO. LTD.) * page 91, line 13 - line 21 * * page 96, line 4 - line 10 *	2-4	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	US-A-4 596 766 (R.NEMORI ET AL) * abstract * * column 3, line 28 - line 31 *	2-4	G03C
A	RESEARCH DISCLOSURE, no. 149, September 1976, HAVANT GB pages 31 - 32; JULIA S. TAN: 'polymeric antistatic agents' * the whole document *	5	
A	WO-A-8 302 506 (EASTMAN KODAK COMPANY) * abstract * * page 5, line 7 - line 22 *	1	
D,A	US-A-4 610 955 (J.CHEN) * abstract * * column 2, line 26 - line 51 *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 MAY 1992	BOLGER W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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D : document cited in the application
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EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 402 774 (KONICA CORPORATION) * page 3, line 1 - line 4 * *Page 4, polymers8,9* ---	5	
A	GB-A-1 334 429 (KONISHIROKU PHOTO-INDUSTRY CO. LTD.) * page 3, left column, line 18 - line 30 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)

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