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(71) Applicant: **MINNESOTA MINING AND MANUFACTURING COMPANY**
St. Paul, Minnesota 55133 (US)

(72) Inventors:
- **Valsecchi, Alberto**
  I-17016 Ferrania (Savona) (IT)
- **Furlan, Fulvio**
  I-17016 Ferrania (Savona) (IT)
- **Martino, Elio**
  I-17016 Ferrania (Savona) (IT)
- **Di Martino, Sergio**
  I-17016 Ferrania (Savona) (IT)
- **Marinelli, Domenico**
  I-17016 Ferrania (Savona) (IT)

(74) Representative: **Allaix, Roberto, Dr.**
3M Italia S.p.A.,
Intellectual Property Department,
Via Martiri della Libertà 57
17016 Ferrania (Savona) (IT)

(54) Antistatic film bases and photographic elements comprising said antistatic film bases

(57) In one embodiment, the invention is directed to a polymeric film base at least one side of which is coated with an antistatic layer comprising (1) the reaction product of (a) a water-soluble, electrically conductive polymer containing carboxylic groups and (b) a polyfunctional epoxide crosslinking agent, and (2) a non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant.

In another embodiment, the invention is directed to a photographic element comprising a polymeric film base, a silver halide emulsion layer on said film base, and an antistatic layer which comprises (1) the reaction product of (a) a water-soluble, electrically conductive polymer containing carboxylic groups and (b) a polyfunctional epoxide crosslinking agent, and (2) a non-ionic perfluoroalkyl(ene) polyoxyalkylene surfactant.

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Description

FIELD OF THE INVENTION

The present invention relates to photographic film bases which are provided with antistatic layers, and to light-sensitive photographic elements comprising said film bases.

BACKGROUND OF THE ART

The use of polymeric film bases for carrying photographic layers is well known. In particular, photographic elements which require accurate physical characteristics use polyester film bases, such as poly(ethylene terephthalate) or poly(ethylene naphthalate) film bases. In fact, polyester film bases, when compared with commonly used cellulose ester film bases, are dimensionally more stable and more resistant to mechanical stresses under most conditions of use.

The formation of static electric charges on the film base is a serious problem in the production of photographic elements. While coating the light-sensitive photographic emulsion, electric charges accumulate on the base discharge, producing light which may be recorded as an image on the light-sensitive layer. Other drawbacks which result from the accumulation of electric charges on polymeric film bases are the adherence of dust and dirt and, coating defects.

Additionally, photographic elements comprising light-sensitive layers coated onto polymeric film bases, when used in rolls or reels which are mechanically wound and unwound or in sheets which are conveyed at high speed, tend to accumulate static charges and record the light generated by the static discharges.

The static-related damages may occur not only before the photographic element has been manufactured, exposed and processed, but also after processing when the photographic element including the image is used to reproduce or enlarge the image. Accordingly, it is desired to provide permanent antistatic protection, that is an antistatic protection which retains its effectiveness even after photographic processing.

Several techniques have been suggested to protect photographic elements from the adverse effects of static charges.

Matting agents, hygroscopic materials or electroconductive polymers have been proposed to prevent static buildup, each acting with a different mechanism. However, matting agents cause haze, dust and dirt problems, hygroscopic materials cause sheets or films to stick together or with other surfaces, and electroconductive polymers are not permanent after photographic processing or are not transparent when coated with conventional binders.

US 4,225,665 purports to disclose permanent antistatic layers for photographic elements. Said layers consist essentially of three components: (1) a water-soluble, electrically conductive polymer comprising carboxylic groups, (2) a hydrophobic polymeric binder containing carboxylic groups, and (3) a polyfunctional aziridine crosslinking agent. This composition, however, does not give clear coatings and causes premature reactions among the components prior to coating. US 4,701,403 suggests a costly system of coating the components as two separate coatings to avoid these premature reactions.

US 4,585,730 discloses a photographic element comprising a film base, a silver halide emulsion on one side of the support, and an antistatic layer on the other side of said support, wherein the antistatic layer is coated with an auxiliary gelatin layer containing a conductive polymer, whereby the antistatic properties of the antistatic layer are conducted through said auxiliary layer. Reference is made to US 4,225,665 and 4,701,403 as useful antistatic layers to be coated with the auxiliary layer according to US 4,585,730. This type of two layer construction, however, often suffers from poor adhesion between the two layers during photographic processing.

An antistatic layer coated onto a polymeric film base has been described in EP 486,982. That antistatic layer comprises the reaction product of a copolymer of sodium polystyrene sulfonate and maleic acid (having a weight average molecular weight of 16,700) with a polyfunctional epoxide crosslinking agent. This antistatic layer provides good adhesion of photographic gelatin layers coated over it even during photographic processing.

EP 589,329 describes an improvement of the above mentioned EP 486,982. The antistatic layer described in EP 589,329 comprises a copolymer of a water soluble salt of styrene sulfonic acid and maleic acid having a weight average molecular weight of 100,000 to 350,000 and a water soluble salt of styrene sulfonic acid to maleic acid molar ratio of at least 2:1 up to 9:1.

However, when the subbing layer composition described in the above mentioned EP 589,329 and EP 486,982 is coated on a substrate contaminated by dirt, oils, and the like, these contaminants induce the formation of defects such as voids and craters. Moreover, when a hydrophilic colloid layer, such as an antihalo layer comprising photographic gelatin, is coated on the subbing layer, wider defects called repellency spots are generated in correspondence to the voids and craters.

Accordingly, there is still the need of an antistatic subbing composition which avoids the above mentioned disadvantages.

SUMMARY OF THE INVENTION

In one embodiment, the invention is directed to a polymeric film base at least one side of which is coated with an antistatic layer comprising (1) the reaction product of (a) a water-soluble, electrically conductive polymer containing carboxylic groups and (b) a polyfunctional epoxide crosslinking agent, and (2) a non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant.

In another embodiment, the invention is directed to a photographic element comprising a polymeric film base, a silver halide emulsion layer on said film base, and an antistatic layer which comprises (1) the reaction product of (a) a water-soluble, electrically conductive polymer containing carboxylic groups and (b) a polyfunctional epoxide crosslinking agent, and (2) a non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant.

This antistatic layer may be present as a backing layer on the side of the film base opposite the silver halide emulsion layer, as a subbing layer between the film base and the emulsion layer in a single or double side coated photographic element, and/or as a subbing layer between the film base and a different backing layer.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises an antistatic film base particularly useful for imaging media, especially silver halide photographic media. The film base comprises a polymeric substrate such as a polyester, and especially polyethyleneterephthalate or poly(ethylene naphthalate). Other useful polymeric substrates include cellulose acetates, polyolefins, polycarbonates and the like. The film base has an antistatic layer adhered to one or both major surfaces of the base. A primer layer or subbing layer may be used between the base itself and the antistatic layer as is known in the art. Priming and subbing layers are, in fact, generally considered to be part of the base itself unless specifically excluded in the description (e.g., unsubbed polyester). Primer and subbing compositions are well known in the art and polymers of vinylidene chloride often comprise the primer composition of choice for photographic elements.

The antistatic layer of the present invention comprises (1) the reaction product of (a) a water-soluble electrically conductive polymer having carboxylic groups and (b) a polyfunctional epoxide crosslinking agent, and (2) a non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant.

The component (a) of the antistatic layer of the present invention is preferably a water-soluble (e.g., soluble in water at room temperature for at least 5% in weight, preferably for at least 10%) electrically conductive hydrophilic copolymer having monomer units comprising:

(a') a -SO_3M substituted ethylenically unsaturated monomer where M is H^+, NH_4^+, monovalent metal cation (e.g., Na^+, K^+, or Li^+) or $N(R)_4^+$, where R is an alkyl group having 1-4 carbon atoms, and
(b') an ethylenically unsaturated comonomer containing carboxylic groups, the molar ratio of (a') to (b') preferably being 1:1 to 5:1, and optionally
(c') another ethylenically unsaturated monomer containing no free carboxylic groups.

More preferably, the component (a) is a copolymer of a styrene sulfonate and an ethylenically unsaturated comonomer containing carboxylic groups. Most preferably, the component (a) is a copolymer of sodium styrene sulfonate and maleic acid in a 2:1 to 4:1 mole ratio. The amount of units derived from electrically conductive monomers (a') serves to balance the requirements for antistatic protection with sufficient capability of the copolymer to become crosslinked through the carboxylic groups of units derived from monomers (b'). For example, monomer (a') may be styrene sulfonic acid, vinyltoluene sulfonic acid, α-methyl-styrene sulfonic acid, 2-ethyl-styrene sulfonic acid, 3-acryloyloxypropane-1-sulfonic acid, 3-methacryloyloxypropane-1-sulfonic acid, 2-acrylamido-2-methylpropane-sulfonic acid, 3-methacryloyloxypropane-1-methyl-1-sulfonic acid, acryloylmethane-sulfonic acid, 4-acryloyloxybutane-1-sulfonic acid, 4-acryloyloxybutane-1-sulfonic acid, 2-acryloyloxyethane-1-sulfonic acid, 2-acrylamidopropane-1-sulfonic acid, 2-methacrylamido-2-methylpropane-1-sulfonic acid, 3-methacrylamido-3-methyl-butane-1-sulfonic acid in the form of alkali metal salts thereof, preferably Na or K, or ammonium salts. Monomer (b') may be maleic acid, acrylic acid, methacrylic acid, 2-butenoic acid. Monomer (c'), if present, is to be chosen so as not to negatively affect the electrical conductivity, water solubility and crosslinking capability of the polymers according to the present invention. Examples of monomers (c') are ethylenic monomers (such as isoprene, 1,3-butadiene, vinyl chloride, ethylene, propylene), styrene type monomers (such as styrene, vinyltoluene, α-methylstyrene, 2-ethyl-styrene, 1-vinylnaphthalene), 2-alkenoic acid esters (such methyl, ethyl, propyl, butyl, hexyl esters of acrylic, methacrylic, α-ethylacrylic, α-propylacrylic, 2-butenoic acids), acrylamide monomers (such as acrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-butylacrylamide, N-chloromethylacrylamide) and vinyl acetate.

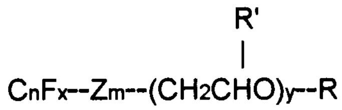
The component (b) of the antistatic layer of the present invention is a polyfunctional epoxide crosslinking agent, that is an organic compound, including a polymeric compound, containing at least two epoxide groups therein. Examples of component (b) are as follows: bis(2,3-epoxypropyl) ether, vinyl cyclohexene dioxide, ethylene bisglycidyl ether, bis(2,3-epoxypropylethyl) ether, hydroquinone bisglycidyl ether, resorcinol bisglycidyl ether, diepoxybutane, diepoxyhexane, bisglycidyl thioether, glycerol trisglycidyl ether, bisglycidyl malonic acid diethyl ester, bisglycidyl sulfone, N,N-bisglycidyl piperazine, trisglycidyl phosphate, 2,4,6-trisglycidyl cyanurate, oxalic acid bisglycidyl ester, succinic acid bisglycidyl ester, bis-(2,3-epoxypropyl)-methyl propyl ammonium p.toluene sulfonate, 1,5-pentane-bis(2,3-epoxypropyl diethyl ammonium methane sulfonate), 2--butyl-1,4-bis(2,3-epoxypropyl dimethyl ammonium perchlorate). These compounds are well known in the art as shown in US Patents Nos. 2,882,250, 3,047,394, 3,189,459, and in FR Patent No. 1,231,056. These compounds may be purchased commercially or synthesized as taught in the above patents.

Specific examples of component (1) of the antistatic layer of the present invention can be found in EP 589,329 and EP 486,982.

The component (2) of the antistatic layer of the present invention is a non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant. In a preferred embodiment, the component (2) of the antistatic layer of the present invention is a non-ionic perfluoroalkyl(ene)polyoxyethylene surfactant.

According to the scope of the present invention, the term "non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant" means a non-ionic surfactant comprising a compound or a mixture of compounds having at least one alkyl or alkylene group of from 3 to 16 carbon atoms wherein the hydrogens are totally replaced by fluorine atoms joined directly or through a linking group to a polyoxyalkylene group comprising from 6 to 24 oxyalkylene groups. Likely, the term "non-ionic perfluoroalkyl(ene)polyoxyethylene surfactant" means a non-ionic surfactant comprising a compound or a mixture of compounds having at least one alkyl or alkylene group of from 3 to 16 carbon atoms wherein the hydrogens are totally replaced by fluorine atoms joined directly or through a linking group to a polyoxyethylene group comprising from 6 to 24 oxyethylene groups.

The preferred non-ionic perfluoroalkyl(ene)polyoxyethylene surfactants can be represented by the following formula:



$$C_nF_x\text{--}Z_m\text{--}(CH_2\overset{\displaystyle R'\\|}{C}HO)_y\text{--}R$$

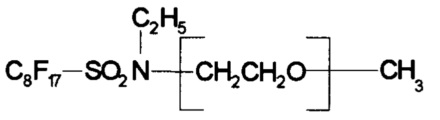
wherein R and R' are, independently, hydrogen or a lower alkyl of from 1 to 4 carbon atoms, Z is a divalent linking group, m is 0 or 1, n is an integer from 3 to 16, x is (n+1) or (n-1), and y is a number from 6 to 24. In a preferred embodiment of the present invention Z can be any of -O-, -S-, -(CH_2)p-, wherein p is an integer from 1 to 6, -NR_1-, -SO-, -SO_2-, NR_1- SO_2-, -SO_2NR_1-, -CO-, -COO-, -$CONR_1$-, NR_1CO-, -NR_1CONR_2-, -$NR_1SO_2NR_2$-, wherein R_1 and R_2, indipendently, can be hydrogen, an alkyl group, and an aryl group.

According to the scope of the present invention when the term "group" is used to describe a chemical compound or substituent, the described chemical material includes the basic group and that group with conventional substitution. Where the term "moiety" is used to describe a chemical compound or substituent only an unsubstituted chemical material is intended to be included.

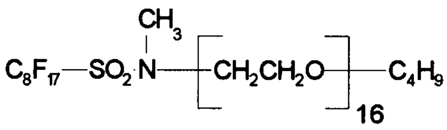
Specific examples of useful non-ionic perfluoroalkyl(ene)polyoxyethylene surfactants are listed below.

$$C_6F_{11}\text{—}SO_2NH\text{—}\left[CH_2CH_2O\right]_8\text{—}C_3H_7 \qquad (1)$$

$$C_5F_{11}\text{—}O\text{—}\left[CH_2CH_2O\right]_{20}\text{—}C_2H_5 \qquad (2)$$

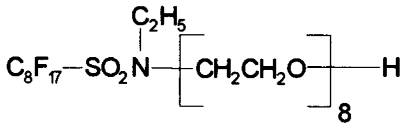


$C_8F_{17}-SO_2\overset{C_2H_5}{\overset{|}{N}}-\left[CH_2CH_2O\right]-CH_3$ (3)



$C_8F_{17}-SO_2\cdot\overset{CH_3}{\overset{|}{N}}-\left[CH_2CH_2O\right]_{16}-C_4H_9$ (4)

$C_8F_{15}-O-\left[CH_2CH_2O\right]_8-CH_3$ (5)



$C_8F_{17}-SO_2\overset{C_2H_5}{\overset{|}{N}}-\left[CH_2CH_2O\right]_8-H$ (6)

$C_{12}F_{23}-C_2H_4-\left[CH_2CH_2O\right]_{12}-C_3H_9$ (7)

$C_{12}F_{23}-O-\left[CH_2CH_2O\right]_{12}-C_3H_9$ (8)

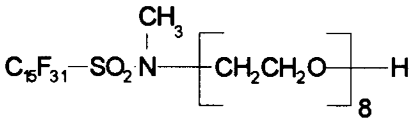
$C_9F_{17}-COO-\left[CH_2CH_2O\right]_{15}-CH_3$ (9)

$C_8F_{17}-\left[CH_2CH_2O\right]_{10}-H$ (10)

$C_{10}F_{19}-\left[CH_2CH_2O\right]_8-H$ (11)

$C_6F_{11}-\left[CH_2CH_2O\right]_6-H$ (12)

$C_3H_7-SO_2NH-\left[CH_2CH_2O\right]_{22}-CH_3$ (13)



$C_{15}F_{31}-SO_2\cdot\overset{CH_3}{\overset{|}{N}}-\left[CH_2CH_2O\right]_8-H$ (14)

$C_5F_{11}-NHSO_2-\left[CH_2CH_2O\right]_{20}-C_2H_5$ (15)

$C_8F_{15}-S-\left[CH_2CH_2O\right]_8-CH_3$ (16)

$C_8F_{17}-SO_2-\left[CH_2CH_2O\right]_8-H$ (17)

$C_8F_{15}-CO-\left[CH_2CH_2O\right]_{12}-C_2H_5$ (18)

$C_6F_{11}-\left[CH_2CH_2O\right]_8-CH_3$ (19)

$C_6F_{13}-\left[CH_2CH_2O\right]_{12}-C_2H_5$ (20)

Prior to being provided on the polymeric base, the antistatic polymer (a) and the crosslinking agent (b) are dissolved in an aqueous solution together with the non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant. The aqueous coating composition can comprise from 1 to 100 g/l, preferably from 5 to 50 g/l of antistatic polymer (a), from 0.1 to 10 g/l, preferably from 0.5 to 5 g/l of crosslinking agent (b), and from 0.01 to 5 g/l, preferably from 0.1 to 1 g/l of non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant. The resulting aqueous coating composition may be coated onto any suitable polymeric photographic base, but the preferred base is polyethyleneterephthalate film which has been subbed with a layer of resin, or layers of resin and gelatin. The antistatic coating is usually provided in coating weight based on the dry weight of from 0.01 g/m^2 to 1 g/m^2. The non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant coating weight of the dry antistatic coating ranges from about 0.001 to 0.5 g/m^2. Lower coating weights usually provide less adequate antistatic protection and higher coating weights usually give less transparent layers. The coating may be performed by conventional coating techniques, such as, for example, air knife coating, gravure coating, doctor roller coating. The antistatic layer of the present invention may also contain other addenda, such as, for example, matting agents, plasticizers, lubricants, surfactants, dyes, and haze reducing agents. The presence of binders is not required, but limited amounts (such as, for example, less than 20%, preferably less than 10% in weight based on the weight of component (a)), of binders, such as gelatin, may be added to the coating composition to improve coating quality of the antistatic layer.

The reaction of (a) and (b) is usually effected during coating and drying of components (a) and (b) onto the polymeric substrate. Heating may be used to accelerate drying and/or the reaction of the components (curing) to form a permanent antistatic layer. Air temperatures of from 20 to 200°C are useful for the drying-curing step, while the preferred range is 50 to 160°C. Catalysts may also be used to speed up the reaction.

The reaction product of (a) and (b) is a crosslinked product, having three-dimensional bonding within the layer. The crosslinking helps provide a permanent antistatic layer which is water-resistant and keeps low molecular weight materials within the component (a) from migrating out of the antistatic layer. Migration is reduced or eliminated into other photographic layers and/or into aqueous processing solutions by the tightening effect of the crosslinking on the internal structure of the antistatic layer.

The presence of non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant(s) provides a good coating quality and avoids the formation of the so-called repellency spot in correspondence of dirt, oil or other contaminants which can be present on the polymeric base.

The imaging elements useful in the present invention may be any of the well-known elements for imaging in the field of graphic arts, printing, medical and information systems. Silver halide, photopolymers, diazo, vesicular image-forming systems may be used, silver halide being preferred.

Typical imaging element constructions of the present invention comprise:

1. The film base with an antistatic layer on one surface and the photosensitive layer or layers, preferably photographic silver halide emulsion layer or layers, on the other surface of the film base. In this construction an auxiliary layer may or may not be present over the antistatic layer. Examples of auxiliary layers include backing gelatin protective layers and backing gelatin antihalation layers.
2. The film base with an antistatic layer on one surface and at least one photosensitive layer adhered to the same surface as the antistatic layer, over the antistatic layer.
3. The film base with antistatic layers on both surfaces of the polymeric base and at least one photosensitive layer on one or both sides of the film base, over said antistatic layers.

Examples of silver halide photographic elements applicable to this invention include black-and-white and color photographic elements.

The silver halide employed in this invention may be any of silver chloride, silver bromide, silver iodide, silver chlorobromide, silver chloroiodide, silver bromoiodide, silver chloroiodobromide, and the like.

The silver halide grains in the photographic emulsion may be regular grains having a regular crystal structure such as cube, octahedron, and tetradecahedron, or the spherical or irregular crystal structure, or those having crystal defects such as twin planes, or those having a tabular form, or combinations thereof.

As the binder or protective colloid for use in the photographic element, gelatin is advantageously used, but other hydrophilic colloids may be used such as gelatin substitutes, collodion, gum arabic, cellulose ester derivatives such as alkyl esters of carboxylated cellulose, hydroxy ethyl cellulose, carboxy methyl cellulose, synthetic resins, such as the amphoteric copolymers described in US Pat. No. 2,949,442, polyvinyl alcohol, and others well known in the art.

The photographic elements utilizing the antistatic layer of this invention have radiation-sensitive silver halide emulsion layers, i.e. silver halide emulsions sensitive to the visible, ultraviolet or infrared light. The silver halide emulsions may be optically sensitized by any of the spectral sensitizers commonly used to produce the desired sensitometric characteristics.

Methods for making such elements, means for sensitizing them to radiation, use of additives such as chemical sensitizers, antifoggants and stabilizers, desensitizers, brightening agents, couplers, hardening agents, coating aids, plasticizers, lubricants, matting agents, high-boiling organic solvents, development accelerating compounds, antistatic agents, antistain agents, and the like are described for example, in **Research Disclosure** Vol. 176, No. 17643, December 1979, Sections I to XIV, and **Research Disclosure** Vol. 308, No. 308119, December 1989.

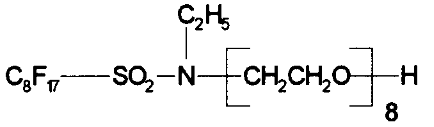
The following examples, which further illustrate the invention, report some experimental data obtained from processes and measurements which are of normal use in the art. Surface resistivity measurements were made using the following procedure: samples of each film were kept in a cell at 21 °C and 25% R.H. for 24 hours and the electrical resistivity was measured by means of a Hewlett-Packard High Resistance Meter model 4329A. The following examples also report three adhesion values: the first is the dry adhesion value and refers to the adhesion of the silver halide emulsion layers and of the auxiliary gelatin layers to the antistatic base prior to the photographic processing; the second value is the wet adhesion value and refers to the adhesion of the above layers to the antistatic base during the photographic processing (developer and fixer); the third adhesion value is the dry adhesion value and refers to the adhesion of the above layers to the antistatic base after photographic processing. In particular, the dry adhesion was measured by tearing samples of the film, applying a 3M Scotch^{TM} 5959 Pressure Sensitive Tape along the tear line of the film and separating rapidly the tape from the film: the layer adhesion was evaluated according to a scholastic method giving a value of 0 when the whole layer was removed from the base, and a value of 10 when no part thereof was removed from the base, and intermediate values for intermediate situations. The wet adhesion was measured by drawing some lines with a pencil point to form an asterisk on the film just taken out from the processing bath and by rubbing on the lines with a finger. In this case the adhesion of the layers was evaluated according to a scholastic method by giving a value of 0 when the layers were totally removed from the base, a value of 10 when no portion thereof was removed, and intermediate values for intermediate cases.

EXAMPLE 1

The following subbing compositions were prepared and coated onto a poly(ethylene terephthalate) film base (PET) resin-subbed on both sides with the terpolymer (vinylidene chloride-itaconic acid-ethylmethacrylate) by the gravure roller coating technique. The amounts of the components reported in the following Table 1 are expressed in grams. All the subbing compositions were coated at a wet coverage of 10 ml/m^2 and coating speed of 60 m/min.

Table 1

Components	Subbing Composition					
	1 Comp.	2 Comp.	3 Inv.	4 Inv.	5 Inv.	6 Inv.
SSMA	40.0	40.0	40.0	40.0	40.0	40.0
EGDGE	4.85	4.85	4.85	4.85	4.85	4.85
Sol. A	-	5.0	5.0	5.0	5.0	5.0
FC-127	1.0	1.0	1.0	1.0	1.0	1.0
FC-170 C	-	-	0.2	0.5	0.8	-
ZONYL™ FSN 100	-	-	-	-	-	0.2
Water	954.15	949.15	949.00	948.35	948.35	949.0

SSMA	Sodium styrenesulfonate-maleic acid (3:1 mole ratio) copolymer (Mw = 16,700)
EGDGE	Ethylenglycol-Diglycidylether
Sol. A	Aqueous solution of N,N-Bis(hydroxyethyl laurylamide) and Monotetradecyl sulfate sodium salt (1.7:1 weight ratio)
FC-127	Glycine N-ethyl-N-((heptadecafluorooctyl)sulfonyl) potassium salt
FC-170 C	 $C_8F_{17}-SO_2-N(C_2H_5)-[CH_2CH_2O]_8-H$
ZONYL™ FSN 100	$C_8F_{17}-[CH_2CH_2O]_{10}-H$

The coating quality was evaluated by scholastic rating from 0 to 10, wherein the higher the score, the better the quality.

The following Table 2 reports the values of surface electrical resistivity and coating quality for the various samples.

Table 2

	Coating Samples					
	1 Comp	2 Comp	3 Inv	4 Inv	5 Inv	6 Inv
Coating Quality	5	8	8	8	8	8
Surface Resistivity Ω/sq	$4*10^9$	$4*10^9$	$1*10^9$	$3*10^9$	$2*10^9$	$3*10^9$

From the results in Table 2 it can be seen how the samples including the Solution A exhibit better coating quality than the reference (Sample 1).

EXAMPLE 2

All the subbings of example 1 were overcoated with a conventional gelatin antihalation layer containing antihalation dyes, a surfactant and a hardener and with a protective layer containing a matting agent, a surfactant and a hardener (Coatings 7,8,9,10,11,12, respectively). The two layers were coated at approximately pH 6. The total gelatin coverage is about 4.5 g/m^2 and the thickness is approximately 4.5 micrometers. A conventional black-and-white silver halide photographic emulsion was coated on the opposite side of each coating. The characteristics of the coatings are reported in the following Table 3. Adhesion values are expressed by scholastic rating (0-10) in which the higher the number, the better the adhesion.

Table 3

	Coating samples					
	7 Comp.	8 Comp	9 Inv.	10 Inv.	11 Inv.	12 Inv.
Surface Resistivity Ω/sq						
- Before processing	$1*10^{11}$	$1*10^{11}$	$1*10^{11}$	$3*10^{11}$	$2*10^{11}$	$3*10^{11}$
- After processing (*)	$3*10^{11}$	$3*10^{11}$	$4*10^{11}$	$5*10^{11}$	$8*10^{11}$	$8*10^{12}$
Adhesion						
- Before processing	10	10	10	10	10	10
- In developer	10	10	10	8	9	5
- In fixer	10	10	10	8	10	6
- After processing	10	10	10	10	10	10
No. of repellency (No./m^2)	31	25	0.07	0.6	2.6	1.9

(*) Processing was made in 3M RDC-5 Developer

The data of Table 3 clearly show that coating samples 9 to 12 of the invention give better results in terms of number of repellency and surface resistivity, while still maintaining a good result in terms of adhesion. Compounds having m=1 show a better value of adhesion then compounds having m=0.

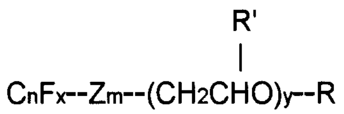
Claims

1. A polymeric film base at least one side of which is coated with an antistatic layer comprising (1) the reaction product of (a) a water-soluble, electrically conductive polymer containing carboxylic groups and (b) a polyfunctional epoxide crosslinking agent, and (2) a non-ionic perfluoroalkyl(ene) polyoxyalkylene surfactant.

2. The polymeric film base according to claim 1, wherein said polymer (a) comprises:

   (a') a -SO_3M substituted ethylenically unsaturated monomer, wherein M is H^+, NH_4^+, metal cation or $N(R)^{4+}$, wherein R is an alkyl group having 1-4 carbon atoms, and
   (b') an ethylenically unsaturated comonomer containing carboxylic groups, the molar ratio of (a) to (b) being 1:1 to 5:1, and optionally
   (c') another ethylenically unsaturated monomer containing no free carboxylic groups.

3. The polymeric film base according to claim 1, wherein said non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant is a perfluoroalkyl(ene) polyoxyethylene surfactant represented by the following formula:



$$C_nF_x\text{--}Z_m\text{--}(CH_2\overset{\overset{R'}{|}}{C}HO)_y\text{--}R$$

wherein R and R' are, independently, hydrogen or a lower alkyl of from 1 to 4 carbon atoms, Z is a divalent linking group, m is 0 or 1, n is an integer from 3 to 16, x is (n+1) or (n-1), and y is a number from 6 to 24.

4. The polymeric film base according to claim 3, wherein said divalent linking group Z is selected from the group consisting of -O-, -S-, -(CH_2)p-, wherein p is an integer from 1 to 6, -NR_1-, -SO-, -SO_2-, NR_1- SO_2-, -SO_2NR_1, -CO-, - COO-, - $CONR_1$-, NR_1CO-, -NR_1CONR_2-, -$NR_1SO_2NR_2$-, wherein R_1 and R_2, indipendently, can be hydrogen, an alkyl group, and an aryl group.

5. The polymeric film base of claim 1, wherein the antistatic layer has a coating weight of 0.01 g/m^2 to 1 g/m^2.

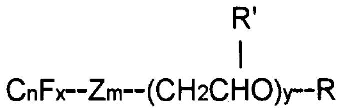
6. The polymeric film base of claim 1, wherein the non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant coating weight of said antistatic layer ranges from about 0.001 to 0.5 g/m^2.

7. A photographic film comprising a silver halide emulsion layer coated on at least one side of a polymeric film base, said polymeric film base having coated on at least one side thereof an antistatic layer, characterized in that said antistatic layer comprises (1) the reaction product of (a) a water-soluble, electrically conductive polymer containing carboxylic groups and (b) a polyfunctional epoxide crosslinking agent, and (2) a non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant.

8. The photographic film of claim 7, wherein said polymer (a) comprises:

(a') a -SO_3M substituted ethylenically unsaturated monomer, wherein M is H^+, NH_4^+, metal cation or $N(R)^{4+}$, wherein R is an alkyl group having 1-4 carbon atoms, and
(b') an ethylenically unsaturated comonomer containing carboxylic groups, the molar ratio of (a) to (b) being 1:1 to 5:1, and optionally
(c') another ethylenically unsaturated monomer containing no free carboxylic groups.

9. The photographic film of claim 7, wherein wherein said non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant is a perfluoroalkyl(ene) polyoxyethylene surfactant represented by the following formula:



$$C_nF_x\text{--}Z_m\text{--}(CH_2\overset{\overset{R'}{|}}{C}HO)_y\text{--}R$$

wherein R and R' are, independently, hydrogen or a lower alkyl of from 1 to 4 carbon atoms, Z is a divalent linking group, m is 0 or 1, n is an integer from 3 to 16, x is (n+1) or (n-1), and y is a number from 6 to 24.

10. The photographic film of claim 9, wherein said divalent linking group Z is selected from the group consisting of -O-, -S-, -(CH_2)p-, wherein p is an integer from 1 to 6, -NR_1-, -SO-, -SO_2-, NR_1- SO_2-, -SO_2NR_1-, -CO-, -COO-, - $CONR_1$-, NR_1CO-, -NR_1CONR_2-, -$NR_1SO_2NR_2$-, wherein R_1 and R_2, indipendently, can be hydrogen, an alkyl group, and an aryl group.

11. The polymeric film base of claim 1, wherein the antistatic layer has a coating weight of 0.01 g/m^2 to 1 g/m^2.

12. The polymeric film base of claim 1, wherein the non-ionic perfluoroalkyl(ene)polyoxyalkylene surfactant coating weight of said antistatic layer ranges from about 0.001 to 0.5 g/m^2.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 95 10 7935

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.6)
D,Y	EP-A-0 589 329 (MINNESOTA MINING AND MANUFACTURING) * page 6, line 17; examples * * page 7, line 26 * ---	1-12	G03C1/85 G03C1/89
Y	US-A-5 028 516 (Y MUKUNOKI ET AL) * column 13, line 42 - column 17, line 23 * * column 25, line 52 - column 29, line 25; claims 1,6 * ---	1-12	
Y	EP-A-0 603 431 (AGFA-GEVAERT) * page 3, line 51 - line 57 * ---	1-12	
Y	EP-A-0 534 006 (AGFA-GEVAERT) * claims * ---	1-12	
A	DE-A-25 13 791 (FUJI) * page 13 * -----	1-12	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 August 1995	Heywood, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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