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Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 552 617 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **93100219.0**

(51) Int. Cl.⁵: **G03C 1/85**, G03C 1/89

(22) Date of filing: **08.01.93**

(30) Priority: **22.01.92 JP 9354/92**

(43) Date of publication of application:
28.07.93 Bulletin 93/30

(84) Designated Contracting States:
DE FR GB NL

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(54) **Photographic light-sensitive material.**

(57) A silver halide photographic light-sensitive material is disclosed, which comprises a support and provided thereon, a silver halide emulsion layer and a photographic component layer other than the silver halide emulsion layer, wherein said photographic component layer contains in admixture a metallic oxide sol and a fluorine-containing copolymer having a unit derived from a fluorine-containing monomer and a unit derived from a hydrophilic monomer other than the fluorine-containing monomer.

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FIELD OF THE INVENTION

The present invention relates to a photographic light-sensitive material, particularly to a photographic light-sensitive material excellent in coating property and improved in antistatic property.

BACKGROUND OF THE INVENTION

Photographic light-sensitive materials are generally composed of a support having an electrical insulating property and photographic component layers such as a photographic emulsion layer, intermediate layer, filter layer, protective layer, subbing layer and backing layer. During manufacture or use, these light-sensitive materials are liable to be electrified due to rubbing or peeling between photographic light-sensitive materials themselves or between a photographic light-sensitive material and another material. When such static electricity is discharged, various troubles arise including fog of a photographic light-sensitive layer which is revealed as static marks after development, and adhesion of foreign matters such as dust. Many methods are known as preventive measures against such troubles. Of them, the most popular and widely used method is to coat the support of a photographic light-sensitive material with an antistatic layer containing an inorganic metal oxide sol dispersion.

However, when coated and dried, such a metal oxide sol dispersion is liable to aggregate or deposit and, thereby, causes coating troubles such as cissing or unevenness and further lowers the coating strength, resistance to scratching, and anti-adhesive property to prevent adjacent photographic films from sticking together.

Addition of a solvent having a relatively high boiling point to a coating system has been tried to prevent such coating troubles and to improve the coating property, but this method is not sufficient in preventing aggregation or deposition and, therefore, cannot be a solution to the problem.

Use of surfactants is also popular as a preventive measure against such coating troubles, but those low molecular weight surfactants which are disclosed in U.S. Pat. Nos. 2,240,476, 3,026,202, 3,068,101, 3,220,847, or 3,415,649 must be used in a large amount to produce substantial effects and, as a result, these deposit on the surface of a coating layer or cause adhesion between a emulsion layer and a backing layer of a photographic light-sensitive material. In addition, these surfactants have problems of exerting bad influences upon photographic properties, such as lower sensitivity and fogs.

Japanese Pat. O.P.I. Pub. Nos. 158222/1979 and 210613/1985 disclose use of fluorine-containing polymers as antistatic agents, but their antistatic properties are not necessarily satisfactory and become lower under low moisture conditions, and when used in a large amount to obtain the intended effect, they produce bad effects on photographic properties, lowering sensitivity and causing fogs.

SUMMARY OF THE INVENTION

The present inventors have made an extensive study to obtain a photographic light-sensitive material excellent in coating property, improved in antistatic property and which does not adversely affect photographic properties and have found that when a fluorine-containing polymer is incorporated in a coating system containing a metal oxide sol dispersion, addition in a small amount is enough to improve the coating property and to make the metal oxide sol dispersion exhibit a sufficient antistatic property. This was a wholly unexpected result judging from the conventional knowledge on the single use of either the metal oxide sol dispersion or the fluorine-containing polymer.

Accordingly, the object of the invention is to provide a photographic light-sensitive material excellent in coating property, in anti-adhesive property high in antistatic property even under low moisture conditions and free from adverse effects upon photographic properties.

The above object of the invention is attained by a photographic light-sensitive material containing, at least in one photographic component layer, a metal oxide sol and a fluorine-containing copolymer made from a polymerizable, fluorine-containing monomer having at least one fluorine atom and a polymerizable hydrophilic monomer.

The invention is hereinafter described in detail.

DETAILED DESCRIPTION OF THE INVENTION

Preferred examples of the metals used in the metal oxide according to the invention include Al, Zn, Ti, Sn, In, W or Y; particularly preferred are Al, Ti, Sn, In or Y.

The metal oxide sol used in the invention is prepared by chemical methods such as hydrolysis of a metal alkoxide or hydrolysis of a metal chloride in an alkaline aqueous solution or by quenching a molten metal oxide in water. Among them, hydrolysis of a metal chloride is preferred.

The average particle size of the metal oxide sol used in the invention is preferably 1 to 100 nm, and more preferably 1 to 50 nm. With regard to a particle size, it is preferable to employ an average particle size obtained through measurement by means of a particle size distribution meter using a precipitation method or a laser diffraction method. The particle size may also be measured by means of an electron microscope, provided that the smallest particle size observed in the field of view is used.

The coating weight thereof is preferably 5 to 500 mg, especially 10 to 200 mg per square meter.

The metal oxide sol used in the invention may contain heterometal elements such as Al, Ga, In, Sn, Sb, Ti, V, Nb, Ta, Ag and Bi; among them, In, Sn, Sb, Nb and Ag are particularly preferred.

The amount of the heterometal element contained is preferably 1 to 25 wt%, more preferably 3 to 20 wt%.

Further, the metal oxide sol according to the invention may contain electrolytes such as inorganic acids (e.g., hydrochloric acid, nitric acid), organic acids including carboxylic acids (e.g., formic acid, acetic acid, propionic acid) and aromatic carboxylic acids (e.g., cinnamic acid), alkali metal hydroxides, and salts thereof (e.g., sodium chloride, sodium acetate). Among them, inorganic acids and carboxylic acids are preferred.

In coating a layer containing the metal oxide sol of the invention, a binder may be contained in such a coating solution.

Any of the polymers used in the usual coating can be employed as a binder; examples thereof include water-soluble polymers such as gelatin, modified gelatins, polyvinyl alcohols, vinyl alcohol copolymers, carboxymethylcellulose, polyacrylic acids, acrylic acid copolymers, polyvinylpyrrolidones, vinylpyrrolidone copolymers, hydroxyethyl acrylate copolymers; cellulose derivatives such as diacetylcellulose, triacetylcellulose, nitrocellulose, acetylbutylcellulose, acetylpropylcellulose, phthaloxycetylcellulose; homopolymers or copolymers of styrene, α -methylstyrene, hydroxystyrene, vinyl acetate, alkyl (alkyl group of 1 to 4 carbon atoms) acrylate, alkyl (alkyl group of 1 to 4 carbon atoms) methacrylate, vinyl chloride, vinylidene chloride; maleic-anhydride-containing copolymers; soluble nylons; soluble polyesters; acetals such as polyvinyl formals, polyvinyl acetals, polyvinyl benzals; and polyurethanes.

In coating the metal oxide sol, there may be used, in addition to the binder, additives such as a matting agent, lubricant and crosslinking agent as well as a surfactant.

The surfactant includes naturally occurring surfactants such as saponins; nonionic surfactants such as alkylene oxide type, glycerin type, glycidol type; and anionic surfactants having an acid group such as a carboxylic acid, sulfonic acid, phosphonic acid, sulfate or phosphate.

As the crosslinking agent, the so-called hardener for photographic gelatin can be used; examples thereof include aldehyde compounds such as formaldehyde, glyoxal; ethyleneimine-group-containing compounds such as mucochloric acid, tetramethylene-1,4-bis(ethyleneurea), hexamethylene-1,6-bis(ethyleneurea); methanesulfonates such as trimethylene-1,3-bismethanesulfonate; active vinyl compounds such as bisacryloylurea, methaxylenevinylsulfonate; active-halogen-containing compounds such as 2-methoxy-4,6-dichlorotriazine, sodium salt of 2-hydroxy-4,6-dichlorotriazine; epoxy-group-containing compounds such as bisphenol glycidyl ether; isocyanate-carboxyl-group-active compounds; and epoxy compounds. Among them, the ethyleneimine-group-containing compounds, methanesulfonates, epoxy compounds and active-halogen-containing compounds are particularly preferred.

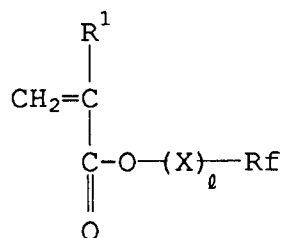
As solvents for dissolving or dispersing the metal oxide sol of the invention, water or organic solvents are used. If necessary, water and an organic solvent may be jointly used. Examples of usable solvents include methanol, ethanol, acetone, methyl ethyl ketone, dimethylformamide, dimethylacetamide, methyl cellosolve, ethyl cellosolve and benzene.

The fluorine-containing copolymer is described hereunder.

The polymerizable, hydrophobic fluorine-containing monomer having at least one fluorine atom is selected according to the polymerization method to be used, but the preferred one is an addition-polymerizing monomer having an ethylenically unsaturated group.

Preferred examples of the addition-polymerizing, fluorine-containing monomer having an ethylenically unsaturated group are those represented by the following formula (I):

Formula (I)



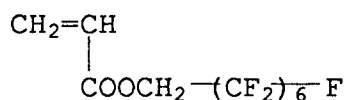
In the formula, R¹ represents a hydrogen or chlorine atom or an alkyl group having 1 to 3 carbon atoms. Rf represents a fluorine-containing alkyl group having 1 to 30 carbon atoms, a fluorine-containing aralkyl or aryl group. X represents a divalent linking group represented by the formula -(R)m-L- or -L-(R)m-, in which R is an alkylene group having 1 to 10 carbon atoms, an arylene or aralkylene group, -L- is an -O-, -S-, -NR²-, -CO-, -OCO-, -SCO-, -CONR²-, -SO₂-, -NR²SO₂-, -SO₂NR²- or -SO- group (R² represents an alkyl group having 1 to 4 carbon atoms) and m is 0 or 1. l is an integer of 0 to 4, preferably 0 or 1. -L- is preferably -NR²-, -CONR²- or -NR²SO₂-. (Wherein R² represents an alkyl group having 1 to 4 carbon atoms).

In Formula (I), R¹ is preferably a hydrogen atom or a methyl group.

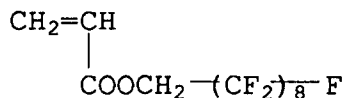
Rf represents an alkyl, aralkyl, aryl or alkylaryl group having 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms in which at least one hydrogen atom is substituted by a fluorine atom; preferred examples thereof include a perfluoromethyl, perfluoroethyl, perfluoropropyl, perfluorohexyl, perfluorooctyl, 2,2,3,3-tetrafluoropropyl, 2,2,3,3,4,4,5,5-octafluoroamyl, 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl, 2,2,2-trifluoroethyl, 2,2,3,3,4,4,4-heptafluorobutyl, 1,1,1,3,3,3-hexafluoro-2-propyl, 1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl, 1,1,2,2-tetrafluoro-2-hydroxyethyl, p-fluorophenyl, p-trifluoromethylphenyl, or 2,3,4,5,6-pentafluoromethylphenyl group.

Examples of the monomer represented by Formula (I) are shown below, but the scope of the invention is not limited to them.

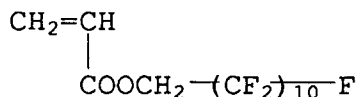
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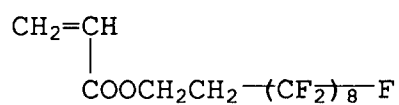
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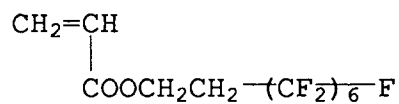
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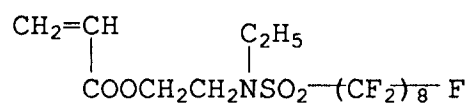
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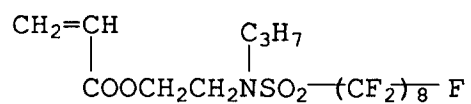
I-5



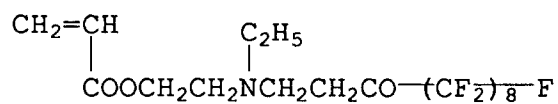
I-6



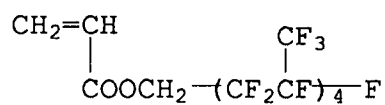
I-7



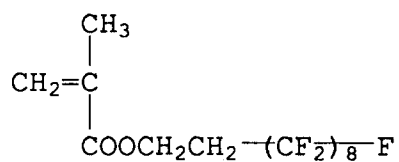
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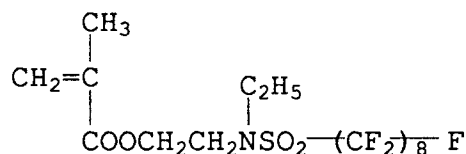
I-9



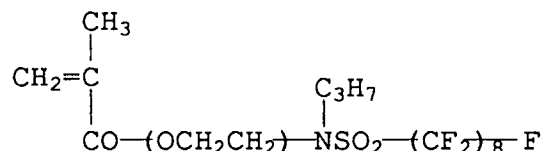
I-10



I-11



I-12



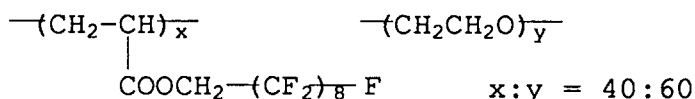
Like the hydrophobic fluorine-containing monomer, a polymerizable hydrophilic monomer is also selected according to the polymerization method to be used, but the preferred one is an addition-polymerizing monomer having an ethylenically unsaturated group. The polymerizable hydrophilic monomer of the invention means a monomer which solubility to water is 1% by weight or more at a temperature of 20°C.

Examples of the addition-polymerizing hydrophilic monomer having an ethylenic unsaturated group include nonionic monomers represented by acrolein, acrylimide, methacrylimide, N-methylolacrylamide, N,N-dimethylaminoethylacrylamide, N,N-dimethylaminopropylacrylamide, hydroxyethyl methacrylate, N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl methacrylate, 2-vinylpyridine, 4-vinylpyridine, 1-vinyl-2-pyrrolidone, 1-vinylimidazole, 1-vinyl-2-methylimidazole; cationic monomers represented by vinylbenzyltrimethyl ammonium salt, vinylbenzyltriethyl ammonium salt, vinylbenzyltripropyl ammonium salt, vinylbenzyltrimethylamine hydrochloride, methacryloxyethyltrimethylethyl ammonium salt, N,N-dimethylaminoethyl methacrylate hydrochloride; and anionic monomers represented by acrylic acid, methacrylic acid, maleic acid, styrenesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid and salts thereof. But usable monomers are not limited to them.

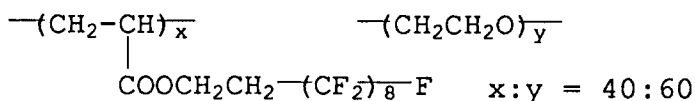
The fluorine-containing copolymer of the invention contains a fluorine-containing monomer of 5 to 70 mol%, and preferably 10 to 50 mol%. The weight average molecular weight of the fluorine-containing copolymer is 3,000 or more, and preferably, 5,000 to 50,000.

The fluorine-containing copolymers of the invention are exemplified below, but the scope of the invention is not limited to them. x:y refers to as mole ratio.

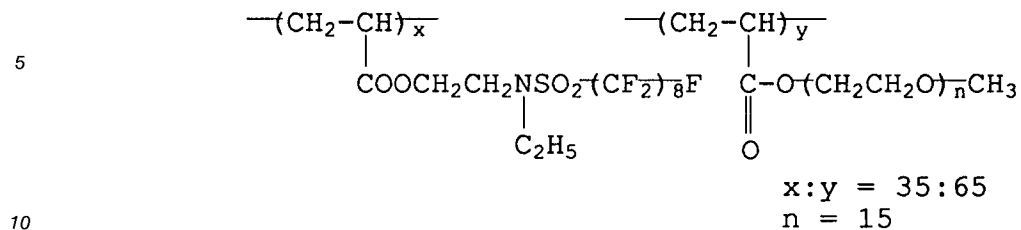
II-1



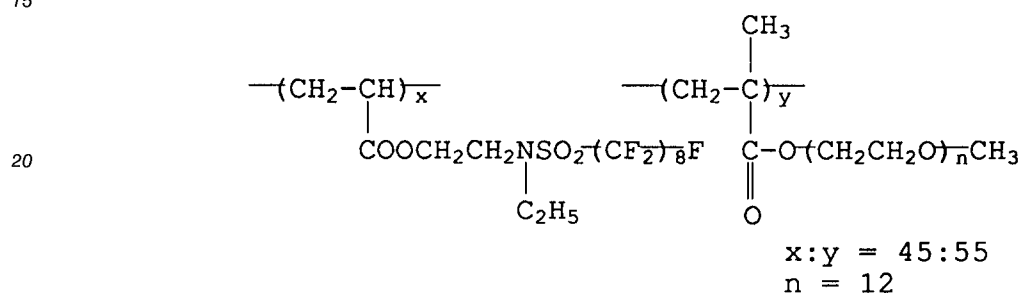
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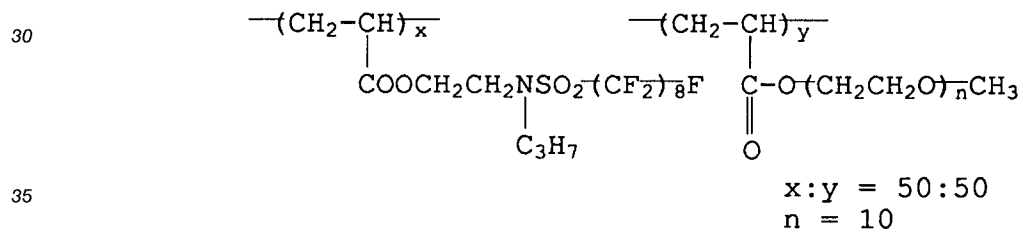
II-3



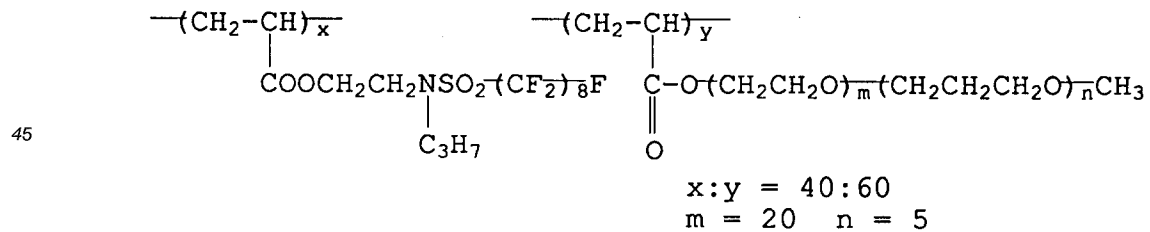
II-4



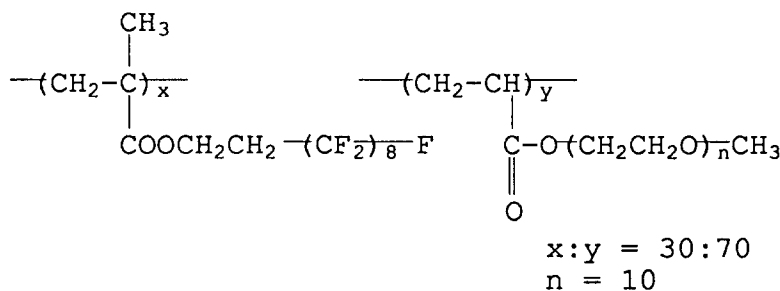
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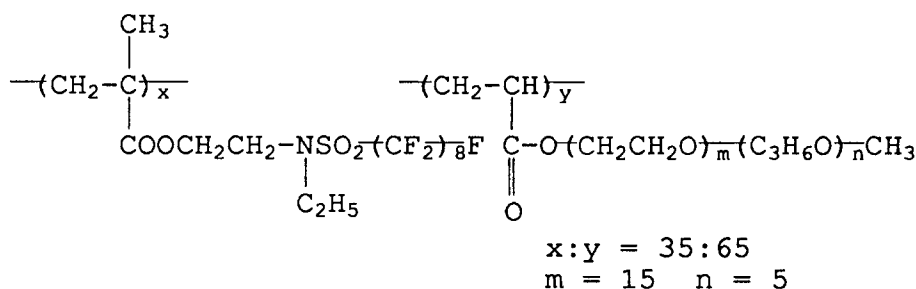
II-6



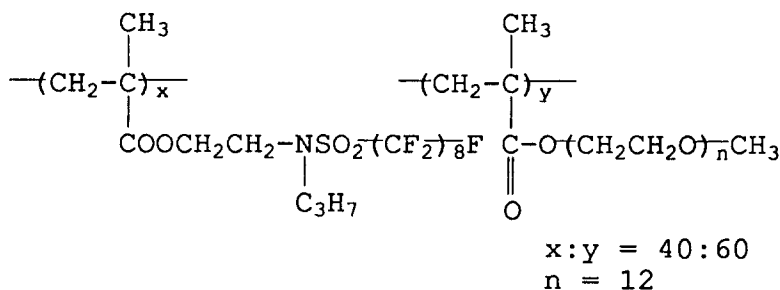
II-7



II-8



II-9



Preferably, the metal oxide sol and the fluorine-containing copolymer are added to layers other than silver halide emulsion layers, for example, to a surface protective layer, intermediate layer, subbing layer or backing layer.

When two or more backing layers are provided, they may be added in any layer.

The addition amount of the fluorine-containing copolymer according to the invention is 0.01 to 3.0 mg, preferably 0.05 to 2.0 mg per square meter of photographic light-sensitive material.

In incorporating the fluorine-containing polymer into a layer of a photographic light-sensitive material, the polymer is dissolved in water or an organic solvent (e.g., methanol, ethanol, acetone, methyl ethyl ketone, ethyl acetate, acetonitrile, dioxane, dimethylformamide, formamide, dimethyl sulfoxide, methyl cellosolve, ethyl cellosolve), or in a mixture thereof, and then incorporated into such a photographic component layer.

As a support of a photographic light-sensitive material which uses the metal oxide sol and the fluorine-containing polymer of the invention, there can be used, for example, films of polyolefin such as polyethylene, polystyrene, cellulose derivatives such as cellulose triacetate, polyesters such as polyethylene terephthalate; baryta paper; synthetic paper; and paper sheets covered with these polymer films on both sides, and analogues thereof.

A layer containing the metal oxide sol and the fluorine-containing polymer of the invention and layers adjacent thereto can be formed by the usual coating method such as curtain coating, reverse roll coating, fountain air doctor coating, slide hopper coating, extrusion coating, or dip coating.

The photographic light-sensitive material according to the invention includes a variety of silver halide light-sensitive materials such as ordinary black-and-white silver halide light-sensitive materials (e.g., black-and-white light-sensitive materials for photographing, black-and-white light-sensitive materials for X-ray photography, black-and-white light-sensitive materials for printing) and ordinary multilayered color light-sensitive materials (e.g., color reversal films, color negative films, color positive films).

EXAMPLES

The invention is hereunder described in detail with examples, but the embodiment of the invention is by no means limited to them. In the examples "parts" is by weight.

Example 1

(Preparation of Metal Oxide Sol)

One thousand parts of stannic chloride aqueous solution (Sn: 16.5%), 45 parts of antimony trichloride and 100 parts of hydrochloric acid (HCl: 34.0%) were thoroughly mixed to give a uniform aqueous solution.

This solution was slowly added to 5,420 parts of ammonium bicarbonate aqueous solution (NH_4HCO_3 : 2.5%) with stirring, so that a tin-oxide antimony-oxide gel was obtained.

The resulting gel was filtered off and the gel was washed and filtered repeatedly till chlorine was not found in the gel. Then, 42 parts of aqueous ammonia (NH_3 : 1.0%) and 298 parts of water were added to 100 parts of this purified tin antimony-oxide gel to obtain a gel slurry of pH 10.4, followed by stirring. The tin-oxide antimony sol so prepared had a pH of 10.0, and its average particle size measured with a transmission electron microscope was 6 nm.

A 1st layer having the following composition was coated on one side of a cellulose triacetate film support to a thickness of 20 ml/m² and dried at 90 °C for 3 minutes.

(1st Layer Composition)

Tin-oxide antimony sol	1.2 g
Diacetylcellulose	6 g
Acetone	400 ml
Water	600 ml

Compound of the invention (shown in Table 1)

Subsequently, a 2nd layer having the following composition was coated on the above 1st layer to a thickness of 20 ml/m² and dried at 80 °C for 3 minutes.

(2nd Layer Composition)

Diacetylcellulose	5 g
Acetone	500 ml
Ethyl acetate	500 ml

Further, a coating solution with the following composition was applied to the above layer at a thickness of 20 ml/m² and dried at 95 °C for 5 minutes.

Carnauba wax	8 g
Toluene	700 ml
Methyl ethyl ketone	300 ml

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The coating property was visually examined for each of the samples prepared. The results are given in Table 1.

Further, after conditioning each sample at 23 °C and 20%RH for 24 hours, the surface specific resistance was measured under the same ambient conditions, at an applied voltage of 100 V, with a Tera-ohm-meter VE-30 made by Kawaguchi Denki Co. The results are shown in Table 1.

10

Table 1

Sample No.	1st Layer		Coating Property	Surface Specific Resistance 23 °C, 20%RH
	Compound Added	Amount Added		
1 (Invention)	II-3	0.7 mg/m ²	Good	$5.2 \times 10^{10} \Omega$
2 (Invention)	II-4	0.7 mg/m ²	Good	$6.5 \times 10^{10} \Omega$
3 (Invention)	II-6	0.7 mg/m ²	Good	$7.8 \times 10^{10} \Omega$
4 (Comparative)	II-3	3.5 mg/m ²	Good	$1.2 \times 10^{10} \Omega$
5 (Comparative)	II-3	5.0 mg/m ²	Good	$8.6 \times 10^9 \Omega$
6 (Comparative)	None		Increase in haze and cissing occurred	$7.5 \times 10^{11} \Omega$

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As is apparent from Table 1, when the coating was made without the compound of the invention (sample No. 6), a rise in haze attributed to partial aggregation of the tin-oxide antimony-oxide sol was observed, and the coating property and surface specific resistance were not sufficient, either. On the contrary, when the coating was done using the compound of the invention sample Nos. 1 to 5 had good coating properties. Sample Nos. 4 and 5 adding the compound of the invention in large amounts lowered surface specific resistance.

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Example 2

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The following 1st layer composition was coated on a cellulose triacetate film support, opposite to the subbing layer provided in the usual manner, to a thickness of 20 ml/m² and dried at 90 °C for 3 minutes.

(1st Layer Composition)

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Alumina sol As-100 (made by Nissan Chem.Ind.)	7.5 g
Diacethylcellulose	7.5 g
Acetone	400 ml
Methanol	500 ml
Dimethylformamide	100 ml

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Compound of the invention (shown in Table 2)

Subsequently, a 2nd layer with the following composition was coated on the above 1st layer to a thickness of 20 ml/m² and dried at 80 °C for 3 minutes.

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(2nd Layer Composition)

5

Diacetylcellulose	5 g
SiO ₂ fine particles (average size: 3.0 μm)	0.2 g
Acetone	500 ml
Ethyl acetate	500 ml

10 Further, a silver halide emulsion layer and a protective layer were coated on the subbed side of the support as follows:

There was prepared a blue-sensitive silver iodobromide emulsion (silver iodobromide content: 7 mol%) containing 300 g/mol AgX of gelatin, 2.5×10^{-2} mol/mol AgX of α -pivaloyl- α -(1-benzyl-2,4-dioxymidazoline-3-yl)-2-chloro-5[γ -(2,4-tert-amylphenoxy)butylamido]acetanilide as yellow coupler and 0.02 g/g gelatin of 1,2-bis(vinylsulfonyl)ethane as hardener. This emulsion was coated, on the subbing layer of the support, together with a gelatin solution for protective layer containing an alkali-soluble matting agent (100 mg/m²) comprising 6:4 methyl methacrylate:methacrylic acid copolymer particles having particle sizes from 2 to 4 μm, sodium di-2-ethylhexylsulfosuccinate (0.01 g/m²) as coating aid, and the above hardener (0.02 g/g gelatin), in the order of the emulsion layer and the protective layer. Sample Nos. 6 to 12 were so prepared.

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Evaluation of the Samples

The coating property of the reverse side (the side coated with the 1st and second layers) of each sample was visually examined. Subsequently, after conditioning each sample at 23 °C and 20%RH for 24 hours, the surface specific resistance was measured in the same environmental conditions, at an applied voltage of 100 V, using a Tera-ohm-meter VE-30 made by Kawaguchi Denki Co.

Further, two 5-cm² specimens were cut out from each sample and stored in an environment of 23 °C and 80%RH for 24 hours, keeping the specimens apart from each other. Then, one specimen was placed upon the other specimen by bringing its nonlight-sensitive protective layer in contact with the outermost backing layer of the other specimen and they were stored in an environment of 55 °C and 55%RH for 24 hours while they were pressed together under a load of 800 g. After storing, the resistance to adhesion was evaluated by measuring the adhering area when the specimens were peeled off.

The criterion for evaluating the resistance to adhesion was as follows:

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Rating	Adhering Area (%)
A	0 to 40
B	41 to 60
C	61 to 80
D	81 or more

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Each of these unexposed samples was stored at 55 °C for 3 days and then subjected to the usual wedge exposure and to development under the following conditions; subsequently, the sensitivity and fogging of each sample were measured.

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In evaluating the sensitivity, the deviation of sensitivity from the reference sensitivity (at a density of fog + 0.3), which was given by the sensitivity of the control sample (sample No. 12) immediately after coating, was determined and expressed by an absolute value of logE as seen in Table 2, where the effect upon photographic properties becomes smaller as the deviation from the reference sensitivity decreases.

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Development Process (38 ° C)	
Color developing	3 min 15 sec
Bleaching	6 min 30 sec
Washing	3 min 15 sec
Fixing	6 min 30 sec
Washing	3 min 15 sec
Stabilizing	1 min 30 sec
Drying	

Composition of the processing solution used in each process was as follows:

[Color developer]

4-Amino-3-methyl-N-ethyl-(β -hydroxyethyl)-aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine 1/2sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
Water was added to make 1 liter.	

[Bleach]

Ammonium ferric ethylenediaminetetracetate	100.0 g
Diammonium ethylenediaminetetracetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 ml
Water was added to make 1 liter, and the pH was adjusted to 6.0 with aqueous ammonia.	

[Fixer]

Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasilicate	2.3 g
Water was added to make 1 liter, and the pH was adjusted to 6.0 with acetic acid.	

[Stabilizer]

Formalin (37% aqueous solution)	1.5 ml
Koniducks (made by Konica Corp.)	7.5 ml
Water was added to make 1 liter.	

The coating property of the reverse side, surface specific resistance, resistance to adhesion, fogging after storing, and sensitivity after storing are summarized in Table 2.

Table 2

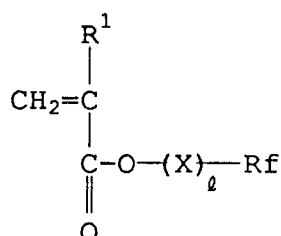
Sample No.	Reverse 1st Layer Compound Amount Added	Coating Property	Surface Specific Resistance 23°C, 20%RH	Resistance to Adhesion	Photographic Properties after Storing	
					Fog	Sensitivity
7 (Invention)	II-3 0.6 mg/m ²	Good	3.8×10^{10} W	A	0.20	-0.01
8 (Invention)	II-4 0.6 mg/m ²	Good	4.3×10^{10} W	A	0.20	-0.02
9 (Invention)	II-6 0.6 mg/m ²	Good	5.2×10^{10} W	A	0.20	-0.02
10 (Comparative)	II-3 3.5 mg/m ²	Good	2.1×10^{10} W	B	0.23	-0.15
11 (Comparative)	II-3 5.0 mg/m ²	Good	9.8×10^9 W	C	0.26	-0.27
12 (Comparative)	None	Rise in haze	8.1×10^{11} W	A	0.20	-0.01

As is apparent from Table 2, when the coating was made without using the compound of the invention (sample No. 12), a rise in haze attributed to partial aggregation of the alumina sol was observed and,

moreover, the coating property as well as the surface specific resistance were insufficient. On the contrary, when the compound of the invention was used in appropriate amounts (sample Nos. 7 to 9), the coating property was good, the surface specific resistance was excellent under low moisture conditions, the resistance to adhesion to the emulsion layer was also good, and no adverse effects on photographic properties were observed. However, when the compound of the invention was used in large amounts (sample Nos. 10 and 11), the resistance to adhesion was lowered and photographic properties were adversely affected.

Claims

1. A silver halide photographic light-sensitive material comprising a support and provided thereon, a silver halide emulsion layer and a photographic component layer other than the silver halide emulsion layer, wherein said photographic component layer contains in admixture a metallic oxide sol and a fluorine-containing copolymer having a unit derived from a fluorine-containing monomer and a unit derived from a hydrophilic monomer other than the fluorine-containing monomer.
2. The material of claim 1, wherein said fluorine-containing monomer is a compound represented by the following formula (I):



wherein R^1 represents a hydrogen atom, a chlorine atom or an alkyl group having 1 to 3 carbon atoms; R_f represents a fluorine-containing alkyl group having 1 to 30 carbon atoms or a fluorine-containing aralkyl or aryl group; X represents $-(R)m-L-$ or $-L-(R)m-$ wherein R represents an alkylene group having 1 to 10 carbon atoms, an arylene or aralkylene group, $-L-$ represents an $-O-$, $-S-$, $-NR^2-$, $-CO-$, $-OCO-$, $-SCO-$, $-CONR^2-$, $-SO_2-$, $-NR^2SO_2-$, $-SO_2NR^2-$ or $-SO-$ group where R^2 represents an alkyl group having 1 to 4 carbon atoms and m represents 0 or 1; and L represents an integer of 0 to 4.

3. The material of claim 2, wherein said R^1 in formula (I) represents a hydrogen atom or a methyl group; said L of said X represents $-NR^2-$, $-CONR^2-$ or $-NR^2SO_2-$ where R^2 represents an alkyl group having 1 to 4 carbon atoms; L represents 0 or 1; and R_f in formula (I) represents a perfluoromethyl group, a perfluoroethyl group, a perfluoropropyl group, a perfluorohexyl group, a perfluorooctyl group, 2,2,3,3-tetrafluoropropyl group, 2,2,3,3,4,4,5,5-octafluoroamyl group, 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl group, 2,2,2-trifluoroethyl group, 2,2,3,3,4,4,4-heptafluorobutyl group, 1,1,1,3,3,3-hexafluoro-2-propyl group, 1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl group, 1,1,2,2-tetrafluoro-2-hydroxyethyl group, p-fluorophenyl group, p-trifluoromethylphenyl group or 2,3,4,5,6-pentafluoro-1-methylphenyl group.
4. The material of claim 1, wherein a metal of the metallic oxide includes Al, Ti, In, or Y.
5. The material of claim 1, wherein said photographic component layer contains said fluorine-containing copolymer in an amount of 0.05 to 2.0 mg/m².
6. The material of claim 1, wherein said fluorine-containing copolymer contains a unit derived from a fluorine-containing monomer in an amount of 30 to 50 mol%.
7. The material of claim 1, wherein said another hydrophilic monomer includes (polyethyleneoxy)acrylate, (polyethyleneoxy)methacrylate, (polypropyleneoxy)acrylate, (polypropyleneoxy)methacrylate, (polyethyleneoxypropyleneoxy)acrylate or (polyethyleneoxypropyleneoxy)methacrylate.

8. The material of claim 1, wherein said photographic component layer contains in admixture said metallic oxide sol in an amount of 5 to 500 mg/m² and said fluorine-containing copolymer in an amount of 0.01 to 3.0 mg/m².

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 93 10 0219

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 Y	US-A-4 622 288 (YOKOYAMA ET AL.) * column 6, line 59 - column 7, line 44 * * column 8, line 32 - line 38 * * column 13; example V4 * * column 22, line 18 - line 25 * * column 22, line 44 - line 57 * ---	1-3,5,6 4,7,8	G03C1/85 G03C1/89
Y	GB-A-2 024 440 (FUJI) * claims 1-4 *	7	
D	& JP-A-54 158 222 (FUJI) ---		
Y	PATENT ABSTRACTS OF JAPAN vol. 14, no. 150 (P-1025)(4093) 22 March 1990 & JP-A-20 12 145 (FUJI) 17 January 1990 * abstract * -----	4,8	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C
Place of search THE HAGUE		Date of completion of the search 01 MARCH 1993	Examiner MAGRIZOS S.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			