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(54) Plastic film with antistatic layer and silver halide photographic light-sensitive material using the same.

(57) A plastic film with an antistatic layer and a silver halide photographic light-sensitive material using the film as the support are disclosed. The antistatic layer comprises a water-soluble electric conductive polymer and particles of a hydrophobic polymer, and hardened with a hardening agent. The hydrophobic polymer has a $-SO_3M$ group or a $-OSO_3M$ group, in which M is a hydrogen atom or a cation. A silver halide photographic material using the film having the inventive antistatic layer is excellent in transparency and sufficiently protected from static charge even after processing.

EP 0 391 402 A1

PLASTIC FILM WITH ANTISTATIC LAYER AND SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL USING THE SAME

FIELD OF THE INVENTION

This invention relates to an antistatic layer for plastic film use and, more particularly, to a silver halide photographic light-sensitive material excellent in antistatic characteristics.

BACKGROUND OF THE INVENTION

Generally, the electrification properties of plastic films are so strong that there are many instances where many restrictions are imposed on their application. In silver halide photographic light-sensitive materials, for example, a polyethylene terephthalate support is generally used.

However, such a support is liable to be electrified, especially, in the relatively low humidity conditions. When a high-speed photographic emulsion is coated at a high-speed, or when a high-speed light-sensitive material is exposed to light through an automatic printer and is then processed as in recent years, a measure to counter electrification is particularly essential.

If a light-sensitive material is electrified or statically charged, the discharge may produce a static-mark or may make a foreign matter such as dusts adhere to the light-sensitive material, thereby producing pin-holes or the like, so that the quality of the light-sensitive material may seriously be worsened. When remedying of the above-mentioned troubles, the working efficiency will seriously be lowered. Therefore, an anti- static agent is generally used in light-sensitive materials and, in recent years, a fluorine containing-surfactant, a cationic surfactant, an amphoteric surfactant, a surfactant or high molecular compound containing a polyethylene oxide group, or a polymer having an intramolecular sulfonic acid group or a phosphoric acid group is used.

In particular, it has been getting popular to use a triboelectric series control method in which a fluorine type surfactant is used, and a conductivity improvement method in which an electric conductive polymer is used. For example, Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) Nos. 49-91165/1974 and 49-121523/1974 disclose each the examples of applying an inon-type polymer having an ionic dissociation group to a polymer principal chain.

In the above-mentioned conventional techniques, however, an antistatic ability is sharply dropped after a development process. It may be presumed that the antistatic ability may be lost by carrying out an alkaline developing step, an acidic fixing step, a washing step, and so forth. Therefore, in an instance where a processed film is further used to make a print, such as in the instance of using a graphic arts light-sensitive material, there may arise such a trouble as pin-holes produced by the adhesion of dusts. To try to solve the above-mentioned trouble, Japanese Patent O.P.I. Publication Nos. 55-84658/1980 and 61-174542/1986, for example, made the proposals each for the antistatic layers comprising a water-soluble conductive polymer containing a carboxyl group, a hydrophobic polymer containing a carboxyl group and a multifunctional aziridine. According to the proposed methods, the antistatic ability can be maintained even after completing the whole process, however, the hydrophobic polymer particles are deteriorated in dispersion stability to produce the coagulation thereof in layers, thereby producing the defect that the transparency of the antistatic layer is damaged.

SUMMARY OF THE INVENTION

As the measure to counter the above-mentioned problems, it is an object of the invention to provide an antistatic layer for plastic film use, which is excellent in transparency without any hase.

Another object of the invention is to provide a silver halide photographic light-sensitive material excellent in antistatic property.

The above-mentioned objects of the invention can be achieved with a plastic film having thereon an antistatic layer comprising a water-soluble electric conductive polymer and particles of a hydrophobic polymer, and hardened with a hardening agent, wherein said haydrophobic polymer has a $-SO_3M$ group or

a -OSO_3M group, in which M is a hydrogen atom or a cation, and a silver halide photographic light-sensitive material using the plastic film as the support thereof.

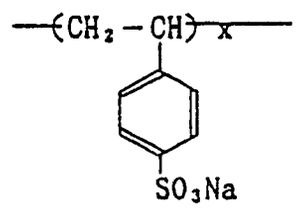
DETAILED DESCRIPTION OF THE INVENTION

The water-soluble conductive polymers of the invention include, for example, a polymer having at least one conductive group selected from the group consisting of a -SO_3M group, a -OSO_3M group in which M is a hydrogen atom or a cation, a quaternary ammonium salt group, a tertiary ammonium salt group, a carboxyl group, and a polyethylene oxide group. Among these groups, a -SO_3M group, a -OSO_3M group, and a quaternary ammonium salt group are preferable. The above-mentioned at least one conductive group is required to be not less than 5% by weight of the polymer. The water-soluble conductive polymer is preferable to contain a hydroxy group, an amino group, an epoxy group, an aziridine group, an active methylene group, a sulfinic acid group, an aldehyde group, or a vinylsulfone group. Each of these groups is referably required to be not less than 5% by weight of the polymer. The molecular weight of each polymer is 3000 to 100000 and, preferably, 3500 to 50000.

The examples of the water-soluble conductive polymer compounds applicable to the invention will be given below. It is, however, to be understood that the invention shall not be limited thereto.

(1)

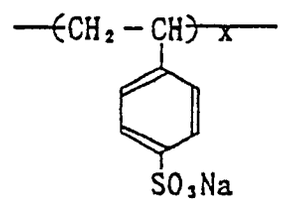
Homopolymer



$\bar{M} \fallingdotseq 20000$

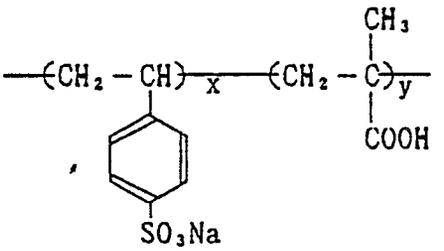
(2)

Homopolymer



$\bar{M} \fallingdotseq 5000$

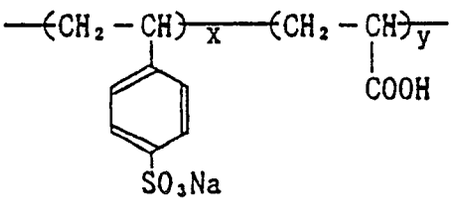
(3)



x:y = 98.5:1.5

$\bar{M}$ ≒ 5000

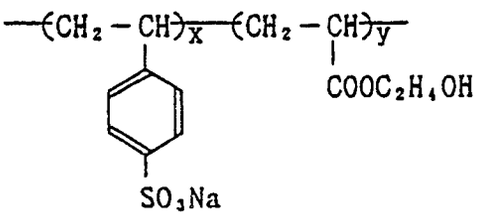
(4)



x:y = 50:50

$\bar{M}$ ≒ 12000

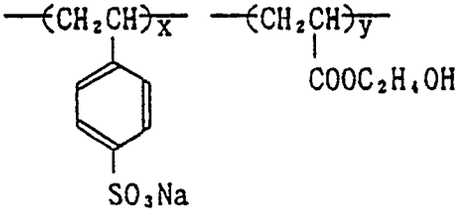
(5)



x:y = 70:30

$\bar{M}$ ≒ 5000

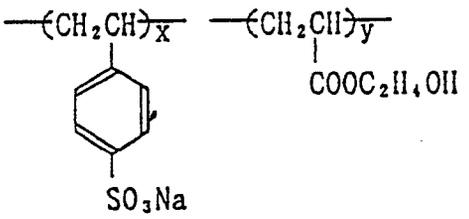
(6)



x:y = 90:10

Mn ≒ 10000

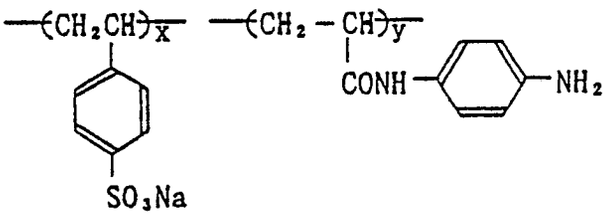
(7)



x:y = 60:40

Mn ≒ 7000

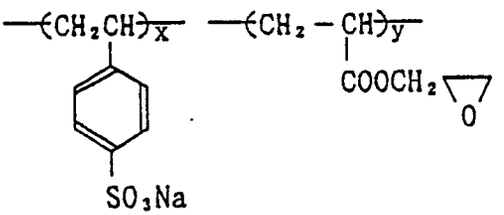
(8)



x:y = 90:10

Mn = 15000

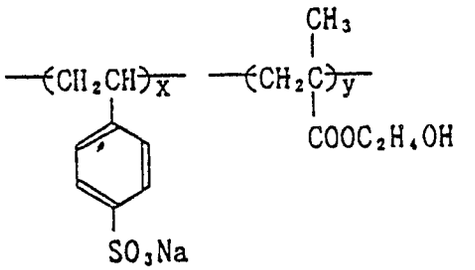
(9)



x:y = 60:40

Mn = 5000

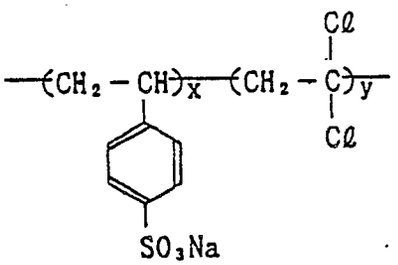
(10)



x:y = 90:10

Mn = 20000

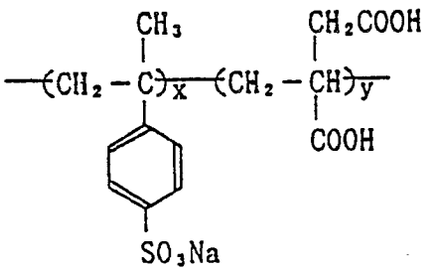
(11)



x:y = 97:3

$\overline{M}$ ≒ 30000

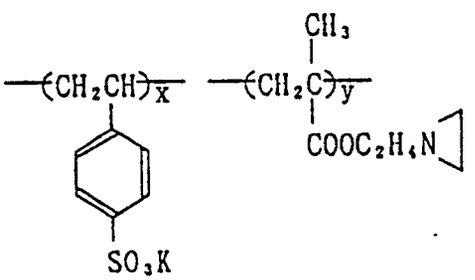
(12)



x:y = 98:2

$\overline{M}$ ≒ 5000

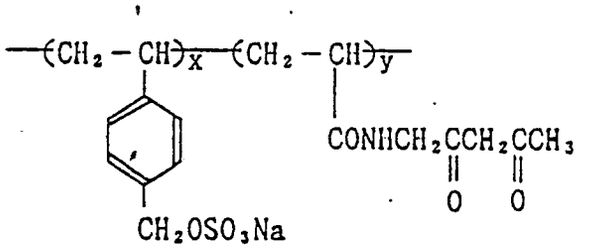
(13)



x:y = 60:40

Mn = 8000

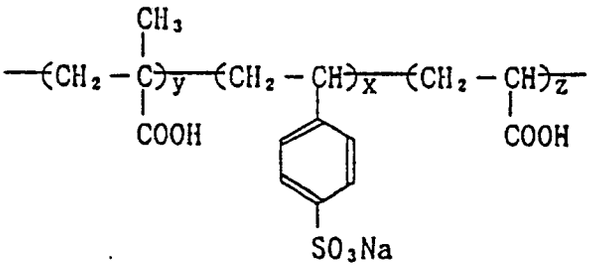
(14)



x:y = 95:5

$\overline{M}$ ≒ 25000

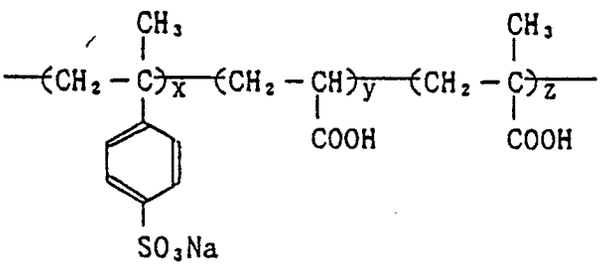
(15)



x:y:z = 80:19:1

$\overline{M}$ ≒ 5000

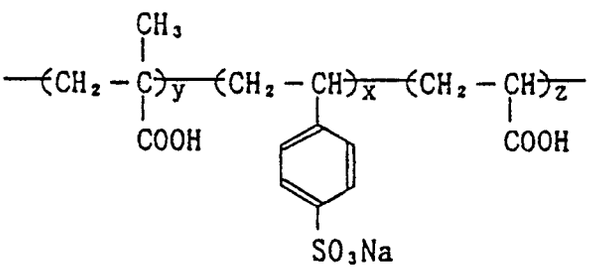
(16)



x:y:z = 70:28:2

$\overline{M}$ ≒ 6000

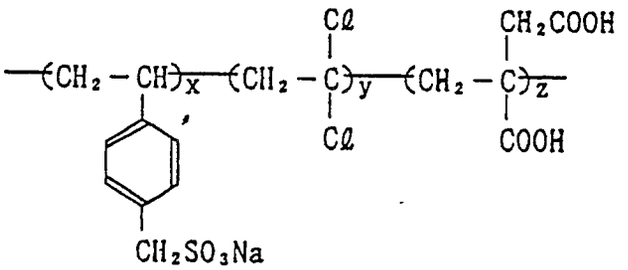
(17)



x:y:z = 85:13:2

$\overline{M}$ ≒ 8000

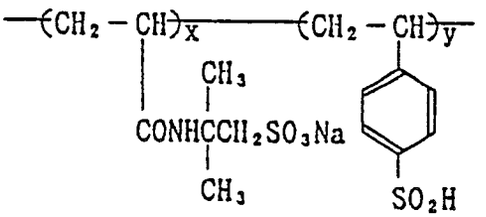
(18)



x:y:z = 80:16:4

$\overline{M}$ ≒ 10000

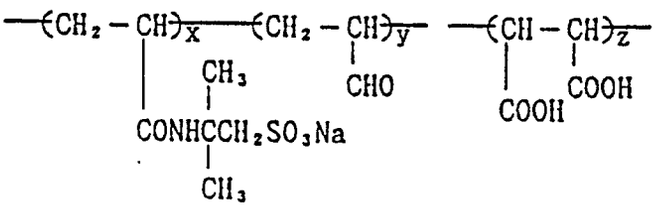
(19)



x:y = 90:10

$\overline{M}$ ≒ 30000

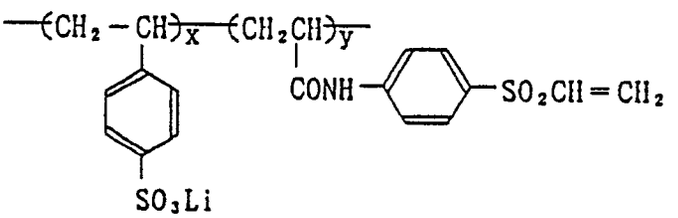
(20)



x:y:z = 85:10:5

$\overline{M}$ ≒ 10000

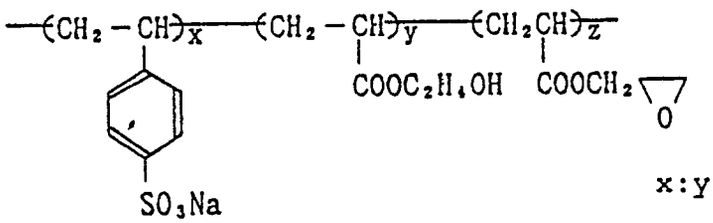
(21)



x:y = 90:10

$\overline{M}$ ≒ 6000

(22)



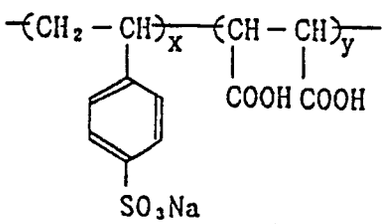
x:y:z = 80:10:10

$\overline{M}$ ≒ 15000

(23) Dextran sulfate

Substitution degree : 2.0 M = 100000

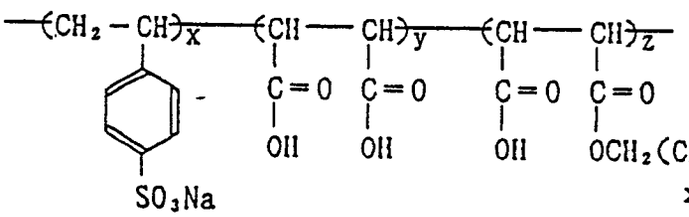
(24)



x:y = 66:34

$\overline{M}$ ≒ 5000

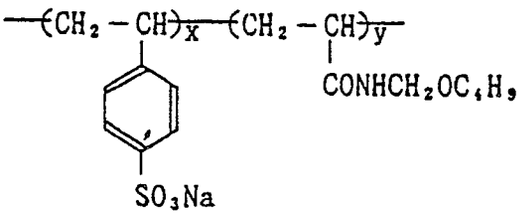
(25)



x:y:z = 50:40:10

$\overline{M}$ ≒ 100000

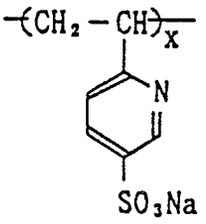
(26)



x:y = 80:20

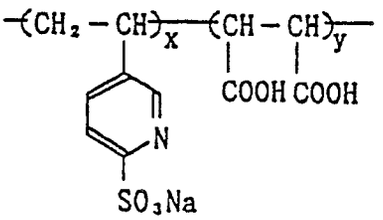
$\overline{M}$ ≒ 50000

(27)



$\overline{M}$ ≒ 100000

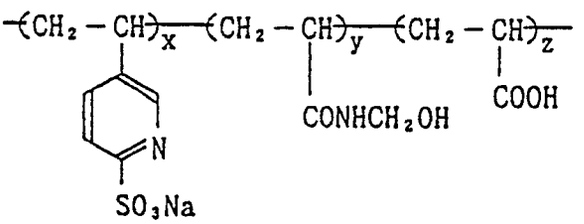
(28)



x:y = 70:30

$\overline{M}$ ≒ 5000

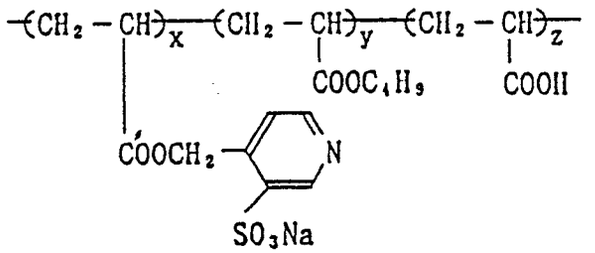
(29)



x:y:z = 55:35:10

$\overline{M}$ ≒ 30000

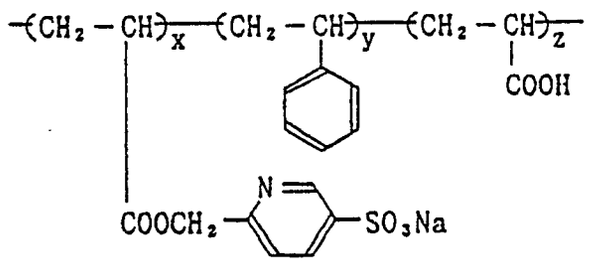
(30)



x:y:z = 50:10:40

$\overline{M}$ ≒ 60000

(31)



x:y:z = 60:10:30

$\overline{M}$ ≒ 60000

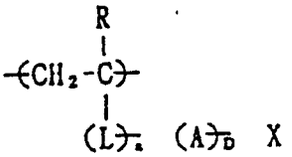
In Examples (1) through (31) given above, x, y, w represent each a mol% of a monomer component, and $\overline{M}$ represents an average molecular weight which means a number average molecular weight in this specification.

The above-given polymers can be synthesized by polymerizing any monomers available on the market or prepared in an ordinary method.

The hydrophobic polymer particles, which are contained in the water-soluble conductive polymer layer of the invention, are to have at least one of a $-SO_3M$ group and a $-OSO_3M$ group, in which M is a hydrogen atom of a cation, and are contained therein in the form of the so-called latexes which are substantially insoluble to water. Such hydrophobic polymers are preferably requied to contain at least one group selected from the group consisting of an N-methylol and its derivative group, an amino group, an epoxy group, an aziridine group, an active methylene group, a sulfinic acid group, an aldehyde group, a vinylsulfone group, and a blocked isocyanate group. The groups given above are contained in a proportion of preferably not less than 1% by weight of the hydrophobic polymers and more preferably not less than 5%. These hydrophobic polymers can be prepared by polymerizing the polymers selected from any combination consisting of a styrene and the derivative thereof, an alkyl acrylate, an alkyl methacrylate, an olefin derivative, a halogenoethylene derivative, an acrylamide derivative, a methacrylamide derivative, a vinyl ester derivative, and an acrylonitrile. Among these hydrophobic polymers, ones containing a styrene derivative an alkyl acrylate or an alkyl methacrylate in a proportion of not less than 30 mol% and, particularly, not less than 50 mol% are preferable.

Among the monomers for introducing a $-SO_3M$ group or a $-OSO_3M$ group into the hydrophobic polymers, those represented by the following Formula I are preferably used.

Formula I



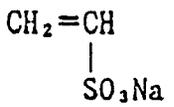
wherein, R represents an alkyl group having 1 to 4 carbon atoms, a hydrogen atom, or a halogen atom. L

represents a divalent group which has 1 to 6 carbon atoms and at least one group selected from the group consisting of a

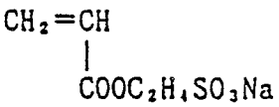
linking groups of $-\overset{\overset{O}{\|}}{C}-$, -NH-, and -O-. The divalent group may be an arylene group or a substituted arylene group. A represents an alkylene or alkenylene group heaving 1 to 12 carbon atoms or an arylene group having 6 to 12 carbon atoms. a, b are each an integer of 0 or 1. X represents $-SO_3M$, or $-OSO_3M$. in which M represents a cation or a hydrogen atom.

The monomers represented by Formula I include preferably the following examples:

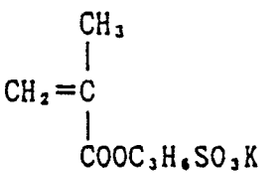
1 .



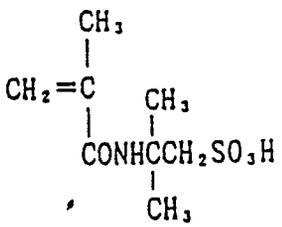
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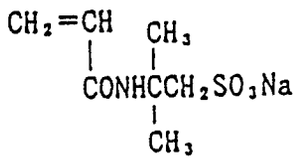
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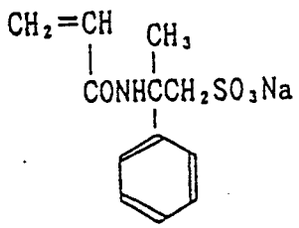
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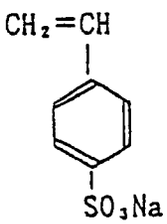
5 .



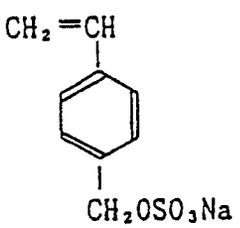
6 .



7 .



8 .



It is preferable to use the monomers having a sulfonic acid group, a sulfuric acid ester group, or the derivatives thereof in a proportion of 0.1 mol% to 20 mol% more preferably, 0.5 mol% to 10 mol%.

There are two methods for making the hydrophobic polymers be in the latex form, one is to emulsion-polymerizing them, and another is to dissolve solid polymers in a low boiling solvent so as to be finely

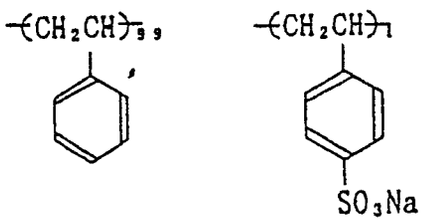
dispersed them in an aqueous medium and the solvent is then distilled off. The emulsion-polymerization method is preferable, because the resulting particles are small and uniform in size.

As a surfactant applied to the emulsion-polymerization, the anionic or nonionic surfactants are preferably used, and such surfactants are used preferably in a proportion of not more than 10% by weight to the monomers used. An excessive amount of the surfactant will cause a conductive layer being clouded.

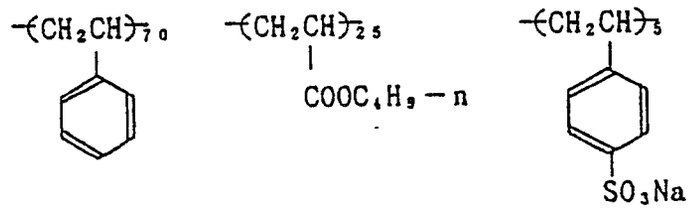
It is good enough when the hydrophobic polymers have a molecular weight of not less than 3000. There is almost no difference in transparency of the conductive layer, even if the molecular weight is varied.

The concrete examples of the hydrophobic polymers of the invention will be given below.

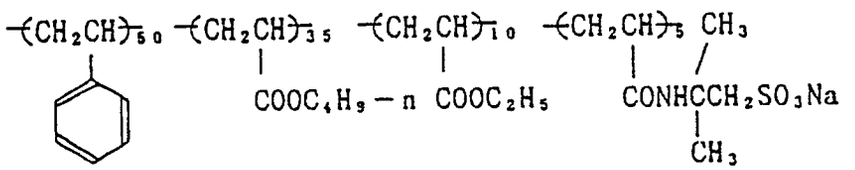
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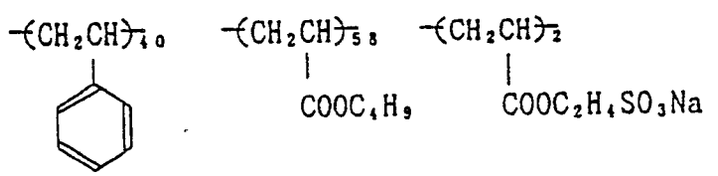
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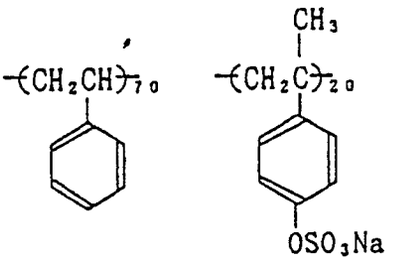
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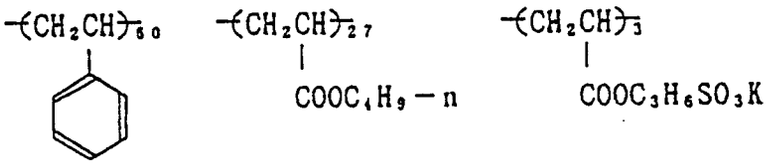
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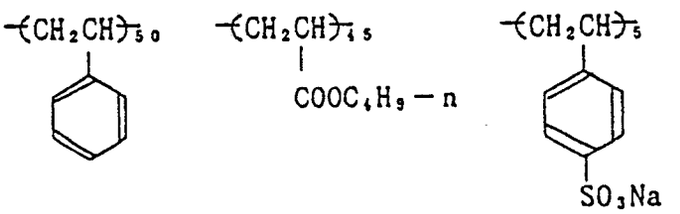
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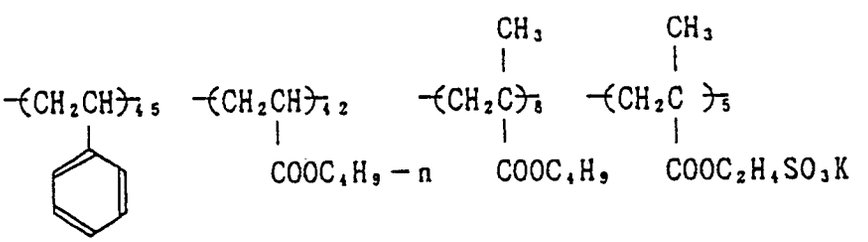
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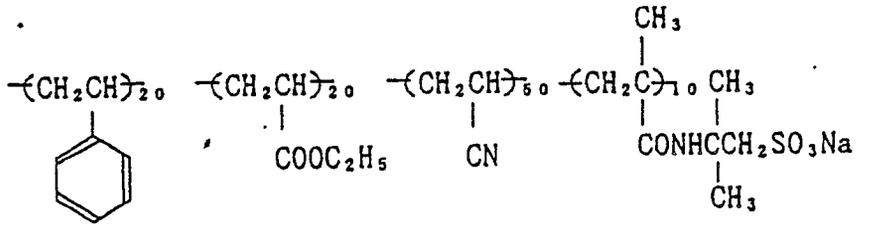
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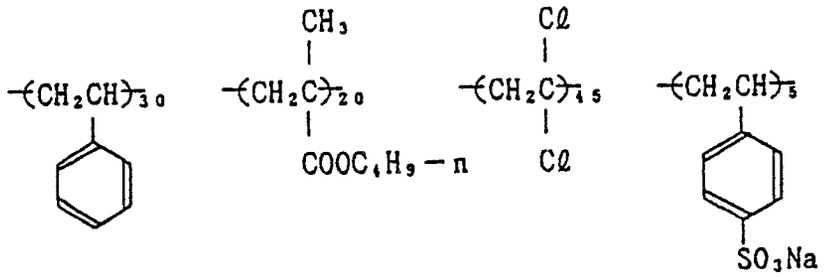
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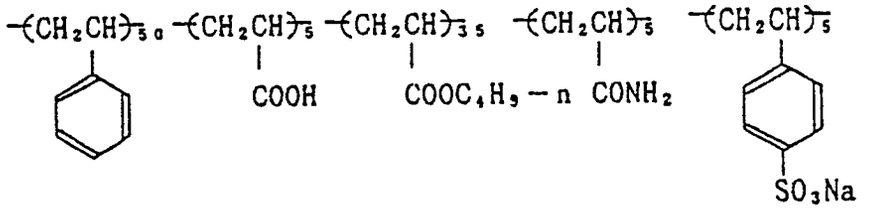
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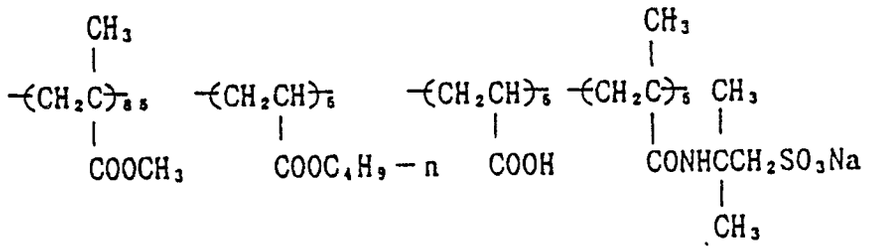
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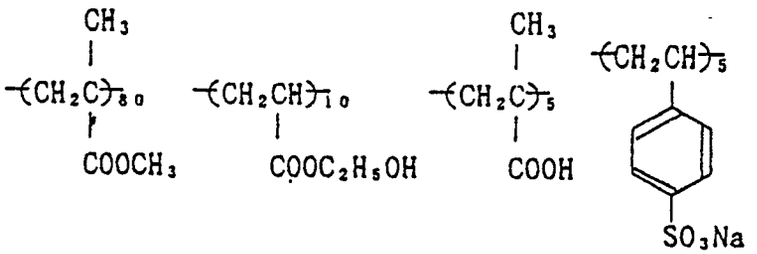
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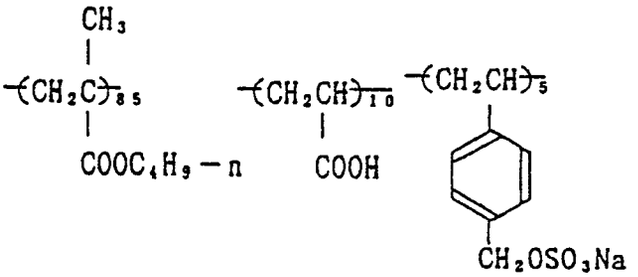
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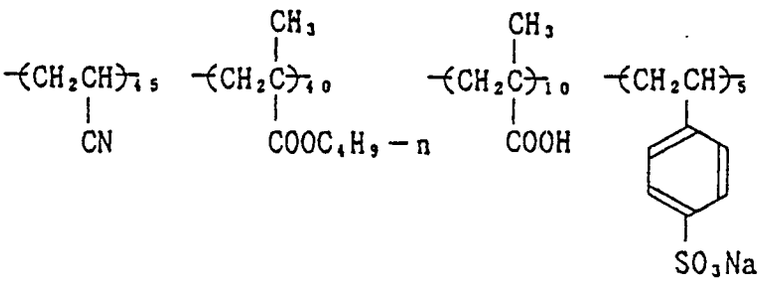
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14.



15.



In the invention, a conductive layer is coated over a transparent support. The supports applicable thereto include any kinds of supports for photographic use. Among them, the preferable ones are those made of polyethylene terephthalate or cellulose triacetate, which are so prepared as to transmit not less than 90% of visible rays of light.

These tranparent supports are prepared in the methods having been well-known in the art. If occasion requires, the supports are allowed to be bluish by adding a small amount of dyes so as not to substantially inhibit light from transmitting through the supports.

After the support is subject to a corona-discharge treatment, it is allowed to coat thereon a subbing layer containing a latex polymer. When treating the corona-discharge, it is more preferable to apply an energy value of 1 mW to 1 KW/m^2•min. In particular, it is preferable to carry out another corona-discharge treatment again between a point of time after coating a latex-subbing layer and a point of time before coating a conductive layer.

The agents for hardening the conductive layers of the invention include, preferably, a multifunctional aziridine compound and, more preferably, a bifunctional or trifunctional one having a molecular weight of not more than 600.

The conductive layers of the invention may be arranged either to the support side closer than a light-sensitive layers or to the opposite side of the support, that is, the back side thereof, with respect to the light-sensitive layers.

This invention can be applied to any light-sensitive material formed on a support, including, for example, a silver halide color light-sensitive material, a radiographic material, and a graphic arts light-sensitive material.

In the silver halide emulsions applicable to the light-sensitive materials of the invention, any silver halides applicable to ordinary silver halide emulsions may be used, such as silver bromide, silver chloride, silver iodobromide, silver chlorobromide, and silver chloroiodobromide. Any silver halide grains may be used in the invention, provided, they are prepared in an acidic method, a neutral method, or an ammoniacal method.

Such silver halide grains may be either those having a uniform silver halide composition distribution therein or core/shell type grains having the different silver halide composition between the inside of the grains and the furface layer thereof. They are further allowed to be either those capable of forming a latent image mainly on the surface thereof or those capable of forming a latent image mainly inside thereof.

The silver halide emulsions applicable to the invention can be stabilized with the use of such a compound as described in, for example, U.S. Patent Nos. 2,444,607, 2,716,062, and 3,512,982, West German DAS Patent Nos. 1,189,380, 2,058,626, and 2,118,411, Japanese Patent Examined Publication No. 43-4133/1968, U.S. Patent No. 3,342,596, Japanese Patent Examined Publication No. 47-4417/1972, West German DAS Patent No. 2,149,789, and Japanese Patent Examined Publication Nos. 39-2825/1964 and 49-13566/1974. These compounds for stabilization preferably include, for example, 5,6-trimethylene-7-hydroxy-S-triazolo(1,5-a)pyrimidine, 5,6-tetramethylene-7-hydroxy-S-triazolo(1,5-a)pyrimidine, 5-methyl-7-hydroxy-S-triazolo(1,5-a)pyrimidine, 5-methyl-7-hydroxy-S-triazolo(1,5-a)pyrimidine, 7-hydroxy-S-triazolo-(1,5-a)-pyrimidine, 5-methyl-6-bromo-7-hydroxy-S-triazolo-(1,5-a)pyrimidine, gallates such as isoamyl gallate, dodecyl gallate, propyl gallate, and sodium gallate, mercaptans such as 1-phenyl-5-mercaptotetrazole, and 2- mercaptobenzthiazole, benzotriazoles such as 5-bromobenz- triazole, and 5-methylbenztriazole, and benzimidazoles such as 6-nitrobenzimidazole.

The silver halide photographic light-sensitive materials and/or the developers, each relating to the invention, may contain an amino compound.

For the purpose of enhancing a developability of light-sensitive material, a developing agent such as phenidone and hydroquinone, and an inhibitor such as benztriazole may be contained in the emulsion side. Or, for the purpose of improving the processability of a processing solution, such a developing agent or inhibitor may be contained in a backing layer.

The hydrophilic colloids particularly advantageous to light-sensitive materials of the invention include, for example, gelatin.

Either alkali-processed and acid-processed gelatins may be applicable. When using ossein gelatin, it is preferable to remove calcium or iron contents. The calcium contents are preferably 1 to 999 ppm and, more preferably, 1 to 500 ppm. The iron contents are preferably 0.01 to 50 ppm and, more preferably, 0.1 to 10 ppm. Such calcium and iron contents may be adjusted by passing an aqueous gelatin solution through an ion-exchanging apparatus.

When developing the silver halide photographic light-sensitive materials relating to the invention, the developing agents applicable thereto include, for example, catechol, pyrogallol and the derivatives thereof, ascorbic acid, chlorohydroquinone, bromohydroquinone, methylehydroquinone, 2,3-dibromohydroquinone, 2,5-diethylhydroquinone, 4-chlorocatechol, 4-phenylcatechol, 3-methoxycatechol, 4-acetylpyrogallol, and sodium ascorbate.

The $HO-(CH=CH)n-NH_2$ type developing agents include an ortho- or para-aminophenol as a typical example and, besides, 4-aminophenol, 2-amino-6-phenylphenol, 2-amino-4-chloro-6-phenylphenol, and N-methyl-p-aminophenyl.

The $H_2N-(CH=CH)n-NH_2$ type developing agents include, for example, 4-amino-2-methyl-N,N-diethylaniline, 2,4- diamino-N,N-diethylaniline, N-(4-amino-3-methylphenyl)- morpholine, and p-phenylenediamine.

The heterocyclic type developing agents include, for example, 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, and 1-phenyl-4-methyl- 4-hydroxymethyl-3-pyrazolidone, 1-phenyl-4-amino-5-pyrazolone, and 5-aminouracil.

The developing agents effectively applicable to the invention include those described in, for example, T.H. James, 'The Theory of Photographic Process', 4th Ed., pp. 291-334, and 'Journal of the American Chemical Society', Vol. 73, p. 3,100, 1951. These developing agents may be used independently or in combination. It is, however, preferable to use them in combination. The effects of the invention are not damaged even when using preservatives including, for example, sulfites such as sodium sulfite and potassium sulfite are used in the developers applicable to develop the light-sensitive materials relating to the invention. Such applicable preservatives include, for example, hydroxylamine and hydrazide com-

pounds. In this case, such a preservative is used in an amount of, preferably, 5 to 500 g and, more preferably, 20 to 200 g per liter of the developer used.

Into such a developer as mentioned above, a glycol may be contained to serve as an organic solvent. The glycols preferably applicable thereto include, for example, ethylene glycol, diethylene glycol, propylene glycol, triethylene glycol, 1,4-butanediol, and 1,5-pentanediol. Among these glycols, diethylene glycol is preferable. Such a glycols may be used in an amount of, preferably, 5 to 500 g and, more preferably, 20 to 200 g per liter of the developer used. The organic solvents may be used independently or in combination.

The silver halide photographic light-sensitive materials relating to the invention are able to display a remarkably excellent preservation stability, when they are processed with a developer as mentioned above.

The pH values of the developers having the above-mentioned compositions are, preferably, 9 to 13 and, more preferably, within the range of 10 to 12 from the viewpoints of the preservability and photographic characteristics of the developers. About the cations contained in a developer, it is preferable when a potassium ion content is more than a sodium ion content, because the developer activity may be enhanced.

The silver halide photographic light-sensitive materials relating to the invention can be processed in various conditions. About the processing temperatures, the developing temperature, for example, is preferably not higher than 50° C and more preferably about 25° C to 40° C. About the developing time, it is general to complete a development within two minutes and more preferably within the range of 10 to 50 seconds to often expect a good result. It is discretionary to adopt other processing steps than the developing step, such as a washing, stopping, stabilizing, fixing and, if required, a prehardening, and neutralizing steps. These discretionary processing steps may be appropriately omitted. Further, these processing steps may be carried out in the so-called manual processing such as a tray or frame processing and the so-called mechanical processing such as a roller or hanger processing, either.

EXAMPLES

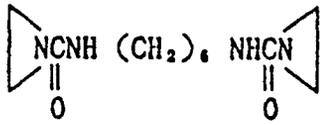
Example-1

A subbed polyethylene terephthalate film was subjected to a corona-discharge treatment and was then coated thereon with an antistatic solution having the following composition in an amount of 10 mℓ/dm², at a coating speed of 33m/min. by means of a roll-fit-coating pan and an air-knife.

Water-soluble conductive polymer shown as A in Table 1 — 6 g/ℓ

Latex of the invention shown as B in Table 1 — 4 g/ℓ

Hardener H



1.5 g/ℓ

The resulting antistatic layer-coated film support was dried at 90° C for 2 minutes and was then heat-treated at 140° C for 90 seconds. Over the antistatic layer, gelatin was coated in an amount of 2.0 g/m², and an transmittance tests was tried. As the hardener for hardening gelatin, formalin and sodium 2,4-dichloro-6-hydroxy-S-triazine were used. Thus obtained samples were subjected to the following transmitance test. The results thereof are shown in Table-1.

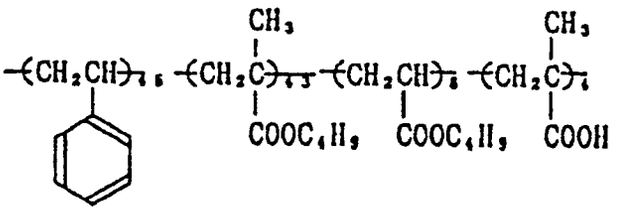
1. Transmittance test

The transmittance of the sample film support was measured by a turbidimeter Model T-2600DA manufactured by Tokyo Denshoku Company. The transmittance thereof is shown interms of percentage.

Table-1

	(A)	(B)	Transmittance (%)
Inventive	(24)	(2)	95
Inventive	(24)	(3)	93
Inventive	(5)	(2)	95
Inventive	(7)	(6)	95
Inventive	(9)	(6)	95
Inventive	(9)	(13)	93
Comparative	(2)	(a)	80

(a) is a comparative latex of a hydrophobic polymer represented by the following formula.



Example-2

<Support with antistatic layer>

A corona-discharge having a power of 30 W/m^2 was applied to a 100 µm thick polyethylene terephthalate support. The support was coated on a side with a subbing solution containing a latex of butyl acrylate- styrene-t-butyl acrylate-hydroxyethyl methacrylate polymer and hexamethylene aziridine hardener, and the antistatic layer of the invention was further coated thereon in the same manner as in Example-1.

The other side of the support, on which a silver halide emulsion layer to be provided, was coated with a subbing solution containing a latex of vinylidene chloride-itaconic acid copolymer.

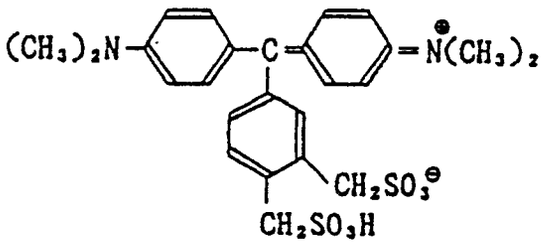
<Backing layer>

Next, onto the lantistatic layer, a backing layer containing the backing dye having the following composition was coated. The gelatin layer was hardened with glyoxal and sodium 1-oxy-3,5-dichloro-S-triazine salt.

Composition of the backing layer	
Hydroquinone	100 mg/m^2
Phenidone	30 mg/m^2
Latex polymer: Butyl acrylate-styrene-acrylic acid copolymer	0.5 g/m^2
Styrene-maleic acid copolymer	100 mg/m^2
Citric acid	40 mg/m^2
Benzotriazole	100 mg/m^2

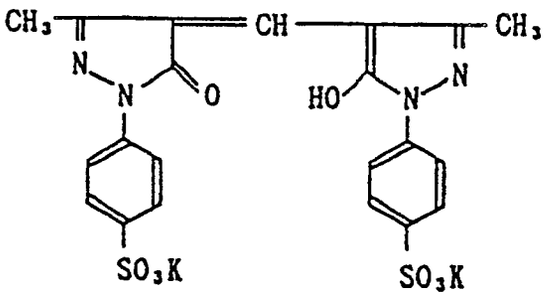
Sodium styrenesulfonate-maleic acid copolymer	200 mg/m^2
Lithium nitrate	30 mg/m^2
Backing dyes a, b, c *	
Ossein gelatin	2.0 g/m^2

* Backing dye a



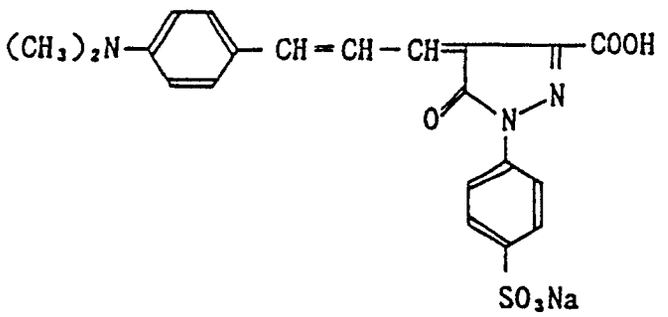
40 mg/m^2

* Backing dye b



30 mg/m^2

* Backing dye c



30 mg/m^2

<Silver halide emulsion>

A silver chloride emulsion containing rhodium of 10^{-5} mols per mol of silver was prepared in a controlled double-jet method under an acidic atmosphere of pH 3.0. Silver chloride grains of the emulsion were grown in the system containing benzyladenine in an amount of 30 mg per liter of an aqueous 1% gelatin solution. After silver and halides were mixed up, 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene was added in an amount of 600 mg per mol of the silver halide used, and then washed and desalted.

Next, after adding 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene in an amount of 60 mg per mol of the silver halide, A sulfur-sensitization was applied. After the sulfur-sensitization, 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene was added as a stabilizer.

<Silver halide emulsion layer>

The additives were added into each resulting emulsion so as to adjust the contents of the additives to be in the quantities given below. The emulsion was coated on each of the above mentioned supports. The emulsion was coated on the side of the support opposite to the side on which the backing layer was provided.

Latex of styrenebutyl acrylate-acrylic acid copolymer	1.0 g/m^2
Tetraphenylphosphonium chloride	30 mg/m^2
Saponin	200 mg/m^2
Polyethylene glycol	100 mg/m^2
Sodium dodecylbenzenesulfonate	100 mg/m^2
Hydroquinone	200 mg/m^2
Phenidone	100 mg/m^2
Sodium styrenesulfonate-maleic acid copolymer (Mw=250,000)	200 mg/m^2
Butyl gallate	500 mg/m^2



30 mg/m^2

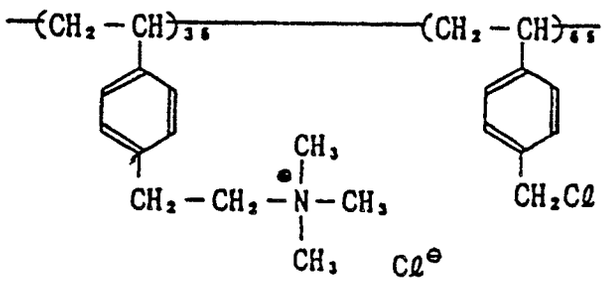
5-methylbenzotriazole	30 mg/m^2
2-mercaptobenzimidazole-5-sulfonic acid	30 mg/m^2
Inert ossein gelatin (with an isoelectric point of 4.9)	1.5 g/m^2
1-(p-acetylamidophenyl)-5-mercaptotetrazole	30 mg/m^2
Silver	2.8 g/m^2

<Protective layer for emulsion layer>

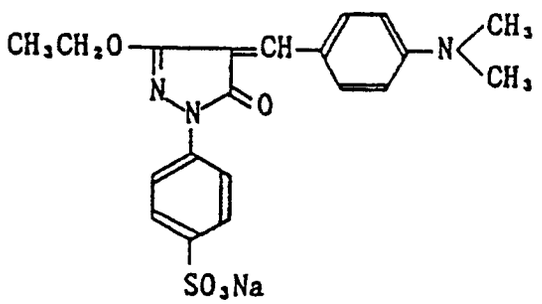
A protective layer for emulsion layer was coated so as to adjust the content to be in the quantity given below.

Fluorinated dioctyl sulfosuccinate	300 mg/m^2
Matting agent: Methyl polymethacrylate (having an average particle-size of 3.5μm)	100 mg/m^2
Lithium nitrate	30 mg/m^2
Acid-processed gelatin (with an isoelectric point of 7.0)	1.2 g/m^2
Colloidal silica	50 mg/m^2
Sodium styrenesulfonate-maleic acid copolymer	100 mg/m^2

Mordant



Dye



The resulting sample was overall-exposed to light and processed with the following developer and fixer. After then, a layer-adhesion transmittance test was tried. Furthe the specific surface resistance of the backing side of the processed sample was measured.

Composition of developer	
Hydroquinone	25 g
1-phenyl-4,4-dimethyl-3-pyrazolidone	0.4 g
Sodium bromide	3 g
5-methylbenzotriazole	0.3 g
5-nitroindazole	0.05 g
Diethylaminopropane-1,2-diol	10 g
Potassium sulfite	90 g
Sodium 5-sulfosalicylate	75 g
Sodium ethylenediaminetetraacetate	2 g
Add water to make	1 liter
Adjust pH with caustic soda to be	11.5

Composition of fixer	
Composition A	
Ammonium thiosulfate (in an aqueous 72.5% solution)	240 mℓ
Sodium sulfite	17 g
Sodium acetate, trihydrate	6.5 g
Boric acid	6 g
Sodium citrate, dihydrate	2 g
Acetic acid (in an aqueous 90w% solution)	13.6 mℓ
Composition B	
Pure water (i.e., ion-exchange water)	17 mℓ
Sulfuric acid (in an aqueous 50w% solution)	3.0 g
Aluminium sulfate (in an aqueous solution having a 8.1 w% $Aℓ_2O_3$ equivalent content)	20 g

In advance, the above-mentioned Compositions A and B were dissolved in order into 500 mℓ of water to make one liter, and then the fixer was used. The pH of the fixer was about 5.6.

Processing conditions		
Processing step	Processing temperature	Processing time
Developing	40° C	8 seconds
Fixing	35° C	8 seconds
Washing	Ordinary temp.	10 seconds

The evaluations were made in the same manner as Example 1, and specific surface resistance was furthe measured. The results thereof are shown in Table-2 given below.

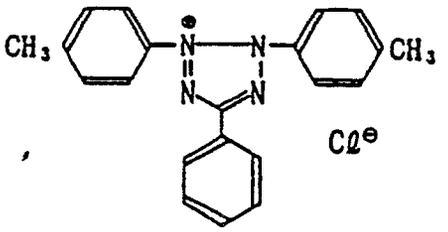
Table-2

	(A)	(B)	Transmittance (%)	Specific surface resistance
Inventive	(24)	(2)	93	$4x10^{10}$
Inventive	(5)	(2)	92	$5x10^{10}$
Inventive	(7)	(6)	93	$5x10^{10}$
Comparative	(2)	(a)	78	$5x10^{10}$

The specific surface resistance by Ω/cm. These values of the specific surface resistance indicate that all of the processed samples are sufficiently protected from static charge.

Further, when the hydrazine compound contained in the emulsion layer was replaced by the following tetrazolium salts, the same effects as in this example were displayed.

Tetazolium compound

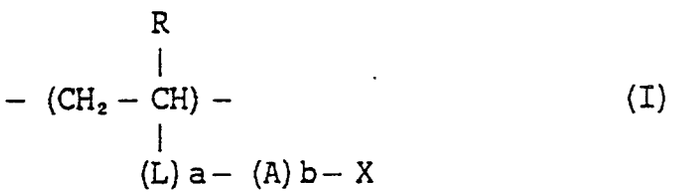


From the results shown in Table-2, it is found that the samples of the invention were very few in the deterioration of antistatic capability even after a development was completed, and excellent in haze-cut characteristics so that the remarkable improvements could be achieved as compared to the comparative sample.

Claims

1. A plastic film having thereon an antistatic layer comprising a water-soluble electric conductive polymer and particles of a hydrophobic polymer, and hardened with a hardening agent, wherein said hydrophobic polymer has a $-SO_3M$ group or a $-OSO_3M$ group, in which M is a hydrogen atom or a cation.

2. The film of claim 1, wherein said hydrophobic polymer is a polymer produced by polymerization of momomers containing including a monomer represented by the following formula I:



(I)

wherein R is a hydrogen atom, a halogen atom or an alkyl group having 1 to 4 carbon atoms, L is a divalent group having 1 to 6 carbon atoms and a group or atoms represented =C=O, -NH- or -O-, A is an alkylene group having 1 to 12 carbon atoms, an alkenylene group having 1 to 12 carbon atoms or an arylene group having 6 to 12 carbon atoms, a and b are each an integer of 0 or 1, and X is a $-SO_3M$ group or a $-OSO_3M$ group, in which M is a hydrogen atom or a cation.

3. The film of claim 2, wherein said hydrophobic polymer is a polymer procuced by polymerising monomers containing said monomer represented by formula I in an amoumt of from 0.1 mol% to 20 mol%.

4. The film of claim 3, wherein said hydrophobic polymer is a polymer produced by polymerising monomers containing said monomer represented by formula I in an amount og from 0.5 mol% to 10 mol%.

5. The film of claim 1, wherein said hydrophobic polymer has an N-methylol or its derivative group, an amino group, an epoxy group, an aziridine group, an active methylene group, sulfinic acid group,. an aldehyde group, a vinylsulfonyl group or a blocked isocyanate group.

6. The film of claim 5, wherein said hydrophobic polymer has an N-methylol or its derivative group, an amino group, an epoxy group, an aziridine group, an active methylene group, sulfinic acid group, an aldehyde group, a vinylsulfonyl group or a blocked isocyanate group in an amount of not less than 5% by weight of said hydrophobic polymer.

7. The film of claim 1, wherein said hydrophobic polymer has a molecular weight of not less than 3000.

8. The film of claim 1, wherein said water-soluble polymer is a polymer having a $-SO_3M$ group, a $-OSO_3M$ group, in which M is a hydrogen atom or a cation, a quaternary ammonium salt group, a tertiary ammonium salt group, a carboxyl group or a polyethylene oxide group.

9. The film of claim 8, wherein said water-soluble polymer has a $-SO_3M$ group, a $-OSO_3M$ group, in which M is a hydrogen atom or a cation, or a quaternary ammonium salt group.

10. The film of claim 8, wherein said water-soluble polymer has a $-SO_3M$ group, a $-OSO_3M$ group, in

which M is ahydrogen atom or a cation, a quaternary ammonium salt group, a tertiary ammonium salt group, a carboxyl group or a polyethylene oxide group in an amount of not less than 5% by weight of said water-soluble polymer.

11. The film of claim 8, wherein said water-soluble polymer further has an N-methylol or its derivative group, an amino group, an epoxy group, an aziridine group, an active methylene group, sulfinic acid group. an aldehyde group, a vinylsulfonyl group or a blocked isocyanate group.

12. The film of claim 11, wherein said water-soluble polymer has an N-methylol group its derivative group, an amino group, an epoxy group, an aziridine group, an active methylene group, a sulfinic acid group, an aldehyde group a vinylsulfonyl group or a blocked isocyanate group in an amount of not less than 5% by weight of said water-soluble polymer.

13. The film of Claim 1, wherein said water-soluble polymer has a molecular weight of from 3000 to 100000.

14. The film of Claim 13, wherein said water-soluble polymer has a molecular weight of from 3500 to 50000.

15. The film of claim 1, said hardening agent is a multi-functional aziridine compound.

16. A silver halide photographic light-sensitive material comprising a silver halide emulsion layer and a plastic film having thereon an antistatic layer comprising a water-soluble electric conductive polymer and particles of a hydrophobic polymer, and hardened with a hardening agent, wherein said hydrophobic polymer has a $-SO_3M$ group or a $-OSO_3M$ group, in which M is a hydrogen atom or a cation.

17. The material of claim 16, wherein said hydrophobic polymer is a polymer produced by polymerization of momomers containing including a monomer represented by the following formula I:

$$-\left(CH_2-\underset{\displaystyle (L)_a-(A)_b-X}{\overset{\displaystyle R}{\underset{|}{\overset{|}{CH}}}}\right)- \qquad (I)$$

wherein R is a hydrogen atom, a halogen atom or an alkyl group having 1 to 4 carbon atoms, L is a divalent group having 1 to 6 carbon atoms and a group or atoms represented $=C=O$, -NH- or -O-, A is an alkylene group having 1 to 12 carbon atoms, an alkenylene group having 1 to 12 carbon atoms or an arylene group having 6 to 12 carbon atoms, a and b are each an integer of 0 or 1, and X is a $-SO_3M$ group or a $-OSO_3M$ group, in which M is a hydrogen atom or a cation.

18. The material of claim 17, wherein said hydrophobic polymer is a polymer procuced by polymerising monomers containing said monomer represented by formula I in an amoumt of from 0.1 mol% to 20 mol%.

19. The material of claim 18, wherein said hydrophobic polymer is a polymer produced by polymerising monomers containing said monomer represented by formula I in an amount og from 0.5 mol% to 10 mol%.

20. The material of claim 16, wherein said hydrophobic polymer has an N-methylol or its derivative group, an amino group, an epoxy group, an aziridine group, an active methylene group, sulfinic acid group, an aldehyde group, a vinylsulfonyl group or a blocked isocyanate group.

21. The material of claim 20, wherein said hydrophobic polymer has an N-methylol or its derivative group, an amino group, an epoxy group, an aziridine group, an active methylene group, sulfinic acid group, an aldehyde group, a vinylsulfonyl group or a blocked isocyanate group in an amount of not less than 5% by weight of said hydrophobic polymer.

22. The material of claim 20, wherein said hydrophobic polymer has a molecular weight of not less than 3000.

23. The material of claim 16, wherein said water-soluble polymer is a polymer having a $-SO_3M$ group, $-OSO_3M$ group, in which M is a hydrogen atom or a cation, a quaternary ammonium salt group, a tertiary ammonium salt group, a carboxyl group or a polyethylene oxide group.

24. The material of claim 23, wherein said water-soluble polymer has a $-SO_3M$ group, $-OSO_3M$ group, in which M is a hydrogen atom or a cation, or a quaternary ammonium salt group.

25. The material of claim 23, wherein said water-soluble polymer has a $-SO_3M$ group, $-OSO_3M$ group, in which M is a hydrogen atom or a cation, a quaternary ammonium salt group, a tertiary ammonium salt group, a carboxyl group or a polyethylene oxide group in an amount of not less than 5% by weight of said water-soluble polymer.

26. The material of claim 23, wherein said water-soluble polymer further has an N-methylol or its derivative group, an amino group, an epoxy group, an aziridine group, an active methylene group, sulfinic acid group. an aldehyde group, a vinylsulfonyl group or a blocked isocyanate group.

27. The material of claim 26, wherein said water-soluble polymer has an N-methylol or its derivative group, an amino group, an epoxy group, an aziridine group, an active methylene group, a sulfinic acid group, an aldehyde group a vinylsulfonyl group or a blocked isocyanate group in an amount of not less than 5% by weight of said water-soluble polymer.

28. The material of Claim 16, wherein said water-soluble polymer has a molecular weight of from 3000 to 100000.

29. The material of Claim 28, wherein said water-soluble polymer has a molecular weight of from 3500 to 50000.

30. The material of claim 16, said hardening agent is a multi- functional aziridine compound.

31. The material of claim 16, wherein said antistatic layer is provided on the side of said film oposite to the side on which said silver halide emulsion layer is provided.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 10 6498

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)
D,Y	US-A-4225665 (F.L.SCHADT) * the whole document *	1, 2	G03C1/89 G03C1/95
Y	GB-A-2001078 (EASTMAN KODAK CO.) * the whole document *	1, 2	
A	US-A-4161407 (G.A.CAMPBELL) * column 3, line 47 - column 3, line 49 * * claim 6 *	5-6, 11-12, 20-22, 26-27	
A	US-A-3411911 (EASTMAN KODAK CO.) * column 5, line 31 - column 5, line 36 * * column 5, line 60 - column 5, line 61 * Examples 1,3	1-4	
A	US-A-3791831 (W.VON BONIN ET AL) * column 6, line 17 - column 6, line 21 *	1	
A	PATENT ABSTRACTS OF JAPAN vol. 10, no. 38 (P-428)(2095) 14 February 1986, & JP-A-60 185947 (MITSUBISHI SEISHI KK) 21 September 1985, * the whole document *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5) G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 JULY 1990	BOLGER W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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