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54 **Packaged silver halide photographic materials and process for their production.**

57 The improved process for manufacturing a packaged silver halide photographic material comprising a step of producing a silver halide photographic material having a support, hydrophilic colloidal layers at least one of which is a light-sensitive silver halide emulsion layer, and an antistatic layer thereon, and a step of packaging said silver halide photographic material, wherein said producing step comprises :

1) providing a hydrophilic colloidal layer on said support; drying said hydrophilic colloidal layer by contacting said hydrophilic colloidal layer with air heated at 35-80°C and/or has a relative humidity of 5-25% for not less than 5 seconds within 5 minutes after the average surface temperature of said hydrophilic colloidal layer becomes lower than a temperature for said drying by 1°C;

2) providing the outermost layer on the side of said support, which has the light-sensitive silver halide emulsion layer, containing 4-80 mg/m² of at least one regular or irregular shaped matting agent having a particle size of not smaller than 4 µm; drying said outermost layer by keeping a temperature of not higher than 19°C to decrease the water to gelatin weight ratio from 800% to 200% and the drying time of not shorter than 35 seconds; and

3) said packaging step comprises maintaining said silver halide photographic material in an atmosphere having a dew point not higher than 16°C until the end of packaging said silver halide photographic material.

The improved packaged photographic material produced by this method is also disclosed.

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This invention relates to packaged silver halide photographic materials (which are hereinafter sometimes referred to simply as "light-sensitive materials") and a process for producing them. More particularly, the present invention relates to packaged light-sensitive materials that experience less deterioration in antistatic property with time and that is also protected against static buildup. The present invention also relates to a process for producing such improved packaged light-sensitive materials.

Plastic films that are customarily used as transparent supports have a great tendency to collect static charges, which often limits the use of those films in practical applications. For example, transparent supports such as polyethylene terephthalate films which are used in silver halide photographic materials are highly prone to collect static charges under low-humidity conditions such as in winter. If light-sensitive materials are charged electrically, discharging electricity will cause an electric shock to operators who handle them or "static marks" will develop in the light-sensitive materials. Further, electrostatically deposited foreign matter such as dust particles can produce pinholes and other surface defects that will substantially deteriorate the quality of the light-sensitive materials.

Prevention of static buildup has become particularly important these days in the photographic industry where it is common practice to coat highly sensitive photographic emulsions at high speed or to expose highly sensitive photographic materials in large volumes with automatic printers.

Under these circumstances, antistatic agents are customarily used in light-sensitive materials and those which are used commonly today include fluorine containing surfactants, cationic surfactants, amphoteric surfactants, surfactants or high-molecular weight compounds that contain a polyethylene oxide group, as well as polymers that contain a sulfonic acid or phosphoric acid group in the molecule. Particularly many proposals have been made with a view to adjusting the triboelectric series with the aid of fluorine containing surfactants or to provide improved conductivity using conductive polymers. See, for example, JP-A-49-91165 (the term "JP-A" as used hereinafter means an "unexamined published Japanese patent application") and JP-49-121523, which disclose examples of using ionic polymers having a dissociative group in the backbone chain.

These prior art techniques, however, have had the problem that their antistatic action is significantly reduced by photographic development. This would be because alkalies used in the development step, acids used in the fixing step, and water used in the washing step deprive the antistatic agents of their effectiveness during processing. If processed films are to be subsequently used in printing as in the case of light-sensitive materials for platemaking, dust particles will collect to produce pinholes and other surface defects on the light-sensitive materials. To avoid this problem, JP-A-55-84658, JP-61-174542, etc. have proposed the use of an antistatic layer comprising a water-soluble conductive polymer having a carboxyl group, a hydrophobic polymer having a carboxyl group, and a polyfunctional aziridine.

It has also been proposed that a conductive metal oxide layer made of tin oxide, indium oxide, etc. be incorporated in the antistatic layer.

The conventional methods described above have the advantage that the desired action of the antistatic layer is retained even after photographic processing. However, the effectiveness of the antistatic layer deteriorates with time and it has been desired to solve this problem. Further, the heart of the prior art antistatic techniques is to increase the conductivity of a light-sensitive material of interest to a sufficient level to provide a path for static electricity to go outside, thereby preventing the buildup of static charges, and no review has ever been made of a total antistatic program that prevents the generation of static electricity and by which any inevitable static electricity is permitted to leak from the article of interest through a conductivity path provided to prevent static buildup.

SUMMARY OF THE INVENTION

The present invention has been achieved under these circumstances and has as an object providing a process for producing a packaged light-sensitive material that experiences less deterioration in antistatic property with time and that is also protected against static buildup. Another object of the present invention is to provide such an improved light-sensitive material in package by said process.

As a result of the intensive studies conducted in order to attain these objects, the present inventors found that the first object of the present invention could be achieved by a process for manufacturing a packaged silver halide photographic material comprising a step of producing a silver halide photographic material having a support, hydrophilic colloidal layers at least one of which is a light-sensitive silver halide emulsion layer, and an antistatic layer thereon, and a step of packaging said silver halide photographic material, wherein said producing step comprises:

- 1) providing a hydrophilic colloidal layer on said support; drying said hydrophilic colloidal layer by contacting said hydrophilic colloidal layer with air heated at 35-80°C and /or has a relative humidity of 5-25% for not less than 5 seconds within 5 minutes after the average surface temperature of said hydrophilic colloidal

layer becomes lower than a temperature for said drying by 1°C;

2) providing the outermost layer on the side of said support, which has the light-sensitive silver halide emulsion layer, containing 4-80mg/m² of at least one regular or irregular shaped matting agent having a particle size of not smaller than 4µm; drying said outermost layer by keeping a temperature of not higher than 19°C to decrease the water to gelatin weight ratio from 800% to 200% and the drying time of not shorter than 35 seconds; and

3) said packing step comprises maintaining said silver halide photographic material in an atmosphere having a dew point not higher than 16°C until the end of packaging said silver halide photographic material. That is a process for producing a packaged light-sensitive material that has hydrophilic colloidal layers, at least one of which is a light-sensitive silver halide emulsion layer, and at least one antistatic layer on a support, which process is characterized in that during the coating and drying of a hydrophilic colloidal layer on at least one side of said light-sensitive material, said layer is brought into contact with air having a temperature of 35 - 80°C and/or a relative humidity of 5 - 25% for at least 5 seconds within 5 minutes from the time when the average surface temperature of the coated layer has rose to a point that is 1°C lower than the drying temperature and, furthermore, the light-sensitive material, after the end of the drying of both sides thereof, is maintained in an atmosphere having a dew point (which is hereinafter sometimes abbreviated to "DP" as required) of no higher than 16°C until the end of the packaging step.

The present inventors continued their studies and found that the generation of static electricity per se could be prevented when the following additional conditions were met: at least one matting agent comprising regular or irregular shaped particles not smaller than 4 µm in size should be contained in an amount of 4-80mg/m² in the outermost layer on the side of a support where a silver halide emulsion layer is formed; the coated surface should have a temperature not higher than 19°C when the weight ratio of water to gelatin in said outermost layer taken as a whole decreases from 800% to 200%; and the drying time over which the weight ratio of water to gelatin in said outermost layer is reduced from 800% to 200% should be at least 35 seconds.

The second object of the present invention can be attained by the improved packaged light-sensitive material that is produced by said process.

DETAILED DESCRIPTION OF THE INVENTION

Photographic layers are usually coated on a light-sensitive material and dried by the following procedure: a coating solution that comprises a gelatin composition is applied onto a support; the applied solution is cooled to solidify in cold air having a dry-bulb temperature of -10 to 15°C; then, the temperature is elevated to dry the coated layer. However, drying under the elevated temperature is primarily for the purpose of enhancing the drying speed and the coated layer is usually brought into contact with air having ambient temperature at the point of time when the drying ends.

In the step of the process of the present invention where at least one of hydrophilic colloidal layers is applied and cooled to become dry by gelling gelatin, the layer is brought into contact with air at 35 - 80°C and/or 5 - 25% r.h. for at least 5 seconds within 5 minutes from the time when the average surface temperature of the coated layer has rose to a point that is 1°C lower than the average temperature of the drying ambient air.

The "time when the average surface temperature of the coated layer has rose to a point that is 1°C lower than the air which it contacts" usually corresponds to the water content of the hydrophilic colloidal composition, for example, a gelatin composition, that is typically within the range of 60 - 20% and, in practice, the drying process can be considered to have ended at that point. The coated layer is brought into contact with air at 35°C - 80°C for at least 5 seconds within 5 minutes from that point. By so doing, the storage stability of the antistatic property of the light-sensitive material could be markedly improved. This would have become possible by complete removal of the residual water in the antistatic layer and it was quite surprising that the storage stability of antistatic action could be markedly improved by proper selection of the drying conditions.

Bringing the light-sensitive material into contact with air at 35 - 80°C corresponds substantially to contact with air having a relative humidity of 5 - 25%. Equally good results are achieved in the present invention by bringing the light-sensitive material into contact with air having a relative humidity of 5 - 25%.

The "time when the coating and drying operations end" as used herein means the time at which the light-sensitive material has been brought into contact with air (e.g. dry air) having a temperature of 35 - 80°C and/or a relative humidity of 5 - 25%.

Bringing the light-sensitive material into contact with air at the time when the drying operation ends is effective for the purposes of the present invention. When a layer is coated and dried on one side of the support and then another layer on the other side, the above-described heat treatment need not be performed in the coating and drying process for both sides of the support and applying said treatment to only one side of the support will suffice. However, in a particularly preferred embodiment, said treatment is performed in the coating and

drying process for both sides of the support.

In order to ship the thus treated silver halide photographic material as the final product, it must be packaged after the coating and drying operations ended for both sides of the support. The objects of the present invention can be attained only when all the steps following the end of the coating and drying of both sides of the light-sensitive material until it is packaged are performed in an environment having a DP (dew point) of no higher than 16°C (with the moisture in the package being also taken into account).

In the practice of the present invention, desired effects are attained by performing the drying operation under the conditions described above and the drying media that can be used are not limited to dry air alone and other suitable media can be employed such as far infrared rays and microwaves.

When air is used as a means of drying the light-sensitive material, term "dry air" as used herein means air that is to be brought into substantial contact with the light-sensitive material, that is supplied for the purpose of drying or controlling humidity, and that is blown directly against the light-sensitive material. This term does not mean air that is present between adjacent turns of the roll of light-sensitive material that has been wound up after coating and drying operations, nor does it mean air that is present between sheets of the light-sensitive material that have been stacked one on another after being cut to a desired size.

The "steps following the end of the coating and drying process until the light-sensitive material is packaged" typically include steps such as winding up, cutting and packaging and sometimes include other steps such as the storage and transport of the light-sensitive material.

The term "air that is to make substantial contact with the light-sensitive material" as used herein means air that is in contact with the light-sensitive material while the latter does not make contact with anything but air. Light-sensitive materials are often transported either in a "bulk" form as they have been wound up onto a roll, or in a stack as individual sheets cut to a desired size are superposed one on another. To take the "bulk" form as an example, one may safely conclude that neither side of the support makes substantial contact with the ambient air in which the bulk is placed as long as the portion of the bulk where adjacent turns of the light-sensitive material contact each other is concerned. Therefore, the following case is included as an embodiment of the invention: after the coating and drying process has been completed under the conditions specified by the present invention, the light-sensitive material is wound up onto a roll while making contact with air having a DP not higher than 16°C; the bulk is then transported through air having a DP not higher than 17°C; and thereafter the bulk is unwound, cut to a desired size and packaged while making contact with air having a DP not higher than 16°C.

The term "packaging" as used herein means protecting the light-sensitive material of interest by sealing it with a material (e.g. in a bag) that is lightfast, moistureproof and preferably heat-resistant.

The outermost layer of a support on the side where a silver halide emulsion layer is formed preferably contains at least one of matting agents comprising regular or irregular shaped particles not smaller than 4 µm in size. As already mentioned, the present inventors found that the drying time over which the weight ratio of water to gelatin in the coated layer was reduced from 800% to 200% and the temperature of the coated surface during this period had unexpected criticality to the purpose of protecting the light-sensitive material against the generation of static electricity. A probable reason for this phenomenon is that under the drying conditions already specified above, the matting agent is highly likely to become exposed from the surface of the outermost layer on the side of the light-sensitive material where a silver halide emulsion layer is formed, whereby the area of the interface at which the light-sensitive material contacts an outside object will decrease considerably.

The temperature of the coated surface during the period over which the weight ratio of water to gelatin decreases from 800% to 200% is expressed by the wet-bulb temperature of drying air and is preferably not higher than 19°C, more preferably not higher than 17°C. The drying time over which the water to gelatin weight ratio is reduced from 800% to 200% is preferably at least 35 seconds.

The matting agent to be used in the present invention may be of any known types including: the particles of inorganic materials such as silica (Swiss Patent No. 330,158), a glass powder (French Patent No. 1,296,995), and alkaline earth metals or carbonates of cadmium, zinc, etc. (British Patent No. 1,173,181); and the particles of organic materials such as starch (U.S. Patent No. 2,322,037), starch derivatives (Belgian Patent No. 625,451 and British Patent No. 981,198), polyvinyl alcohol (Examined Japanese Patent Publication (JP-B) No. 44-3643), polystyrene or polymethyl methacrylate (Swiss Patent No. 330,158), polyacrylonitrile (U.S. Patent No. 3,079,257), and polycarbonates (U.S. Patent No. 3,022,169).

These matting agents may be used either on their own or as admixtures. The shape of the particles of which the matting agents are formed may be regular or irregular. Regular particles are preferably spherical but may assume other forms such as a plate and a cube. Particles no smaller than 4 µm must be contained in the matting agent in an amount of 4 - 80 mg/m², preferably 10 - 40 mg/m². The size of non-spherical matting agents is expressed by the diameter of a sphere having the same volume as that of a particle in the matting agent of interest.

By the expression "a matting agent is contained in the outermost layer" is meant that at least part of the

matting agent need be contained in the outermost layer. If necessary, part of the matting agent may extend beyond the outermost layer to reach the underlying layer.

In order for the matting agent to perform its basic function, part of the matting agent is desirably exposed on the surface. Part or all of the matting agent added may be exposed on the surface. The matting agent may be added either by applying a coating solution that has the matting agent dispersed therein or by spraying the matting agent after a coating solution has been applied but before it is dried. If two or more kinds of matting agents are to be added, the two methods may be employed in combination.

The composition of the antistatic layer to be formed in the present invention is not limited in any particular way but in a typical case it contains a water-soluble conductive polymer, a hydrophobic polymer latex, a curing agent, etc.

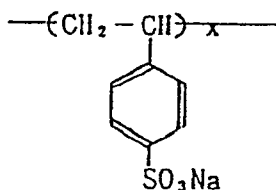
The water-soluble conductive polymer to be contained in the antistatic layer is described below. This water-soluble conductive polymer is a polymer having at least one conductive group selected from among a sulfonic acid group, a sulfate ester group, a quaternary ammonium salt, a tertiary ammonium salt and a carboxyl group. Such conductive groups are preferably present in an amount of at least 5 wt% per polymer molecule. The water-soluble conductive polymer may also contain a hydroxyl 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.

The water-soluble conductive polymer preferably has a molecular weight of 3,000 - 100,000, more preferably 3,500 - 50,000.

Specific, but not-limiting, examples of the compounds that can be used as the water-soluble conductive polymer in the present invention are listed below.

A-1 homopolymer

25

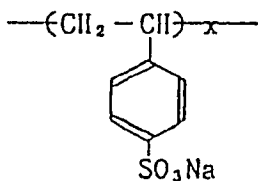


$$M \simeq 6 \times 10^4$$

30

A-2 homopolymer

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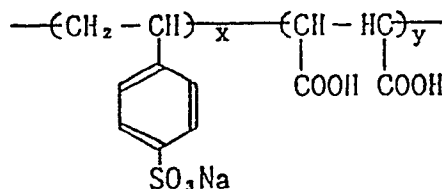


$$M \simeq 7 \times 10^4$$

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A - 3

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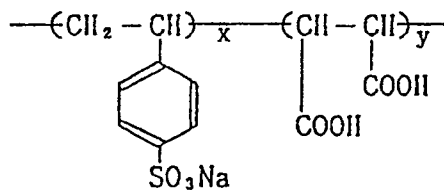


$$X:Y = 67:34$$

$$\bar{M} \simeq 5 \times 10^3$$

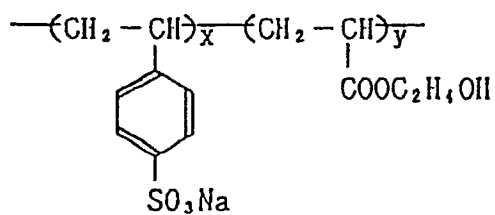
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A - 4

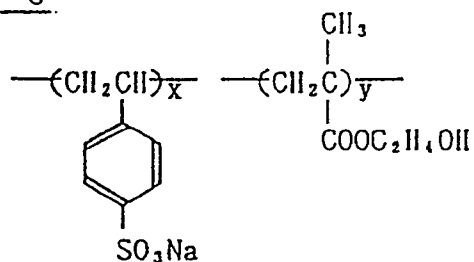
$$x:y=50:50$$

$$\bar{M} \approx 1.2 \times 10^4$$

A - 5

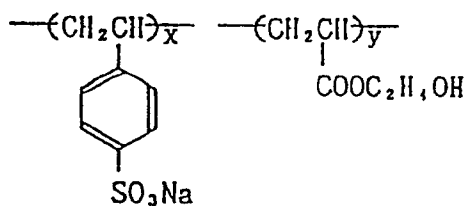
$$x:y=70:30$$

$$\bar{M} \approx 5 \times 10^3$$

A - 6

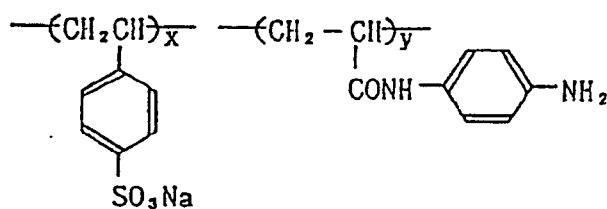
$$x:y=90:10$$

$$M_n = 10^4$$

A - 7

$$x:y=60:40$$

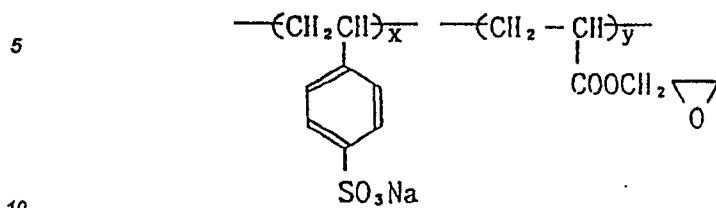
$$M_n = 7 \times 10^3$$

A - 8

$$x:y=90:10$$

$$M_n = 1.5 \times 10^4$$

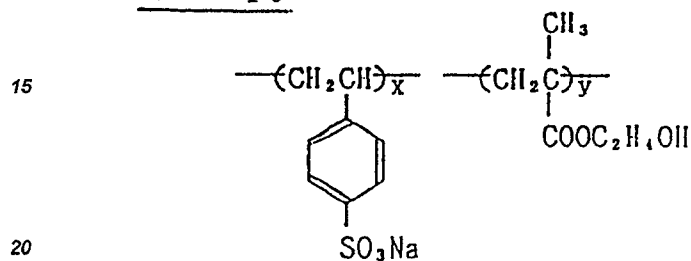
A - 9



$$x:y = 60:40$$

$$M_n = 5 \times 10^3$$

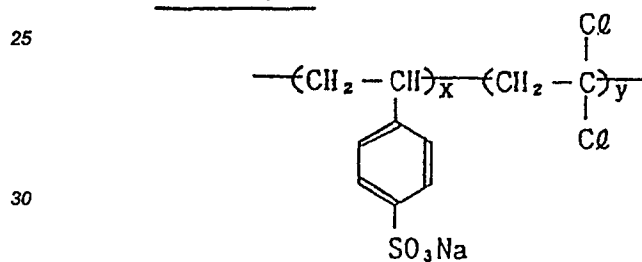
A - 10



$$x:y = 90:10$$

$$M_n = 2 \times 10^4$$

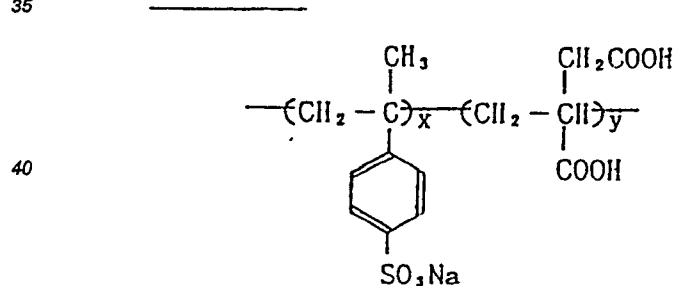
A - 11



$$x:y = 97:3$$

$$\bar{M} \approx 3 \times 10^4$$

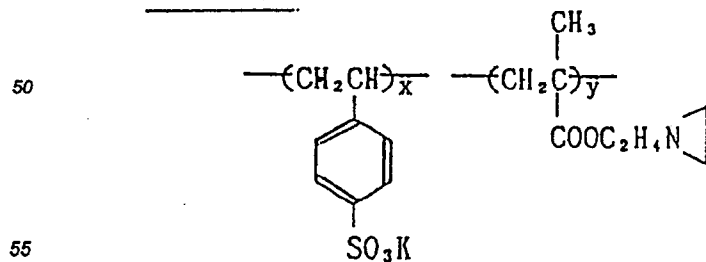
A - 12



$$x:y = 98:2$$

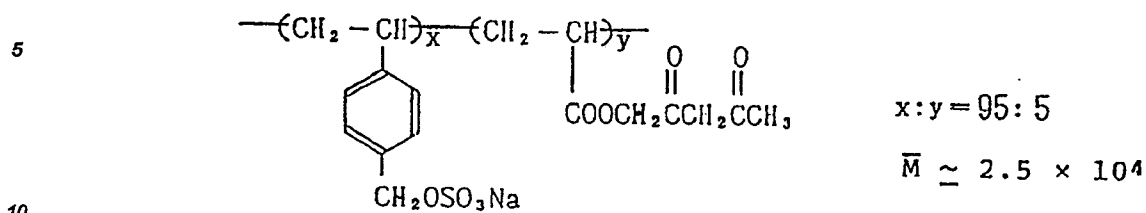
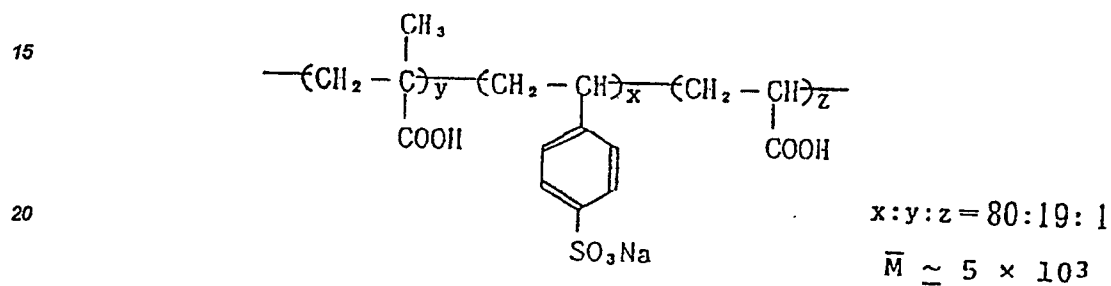
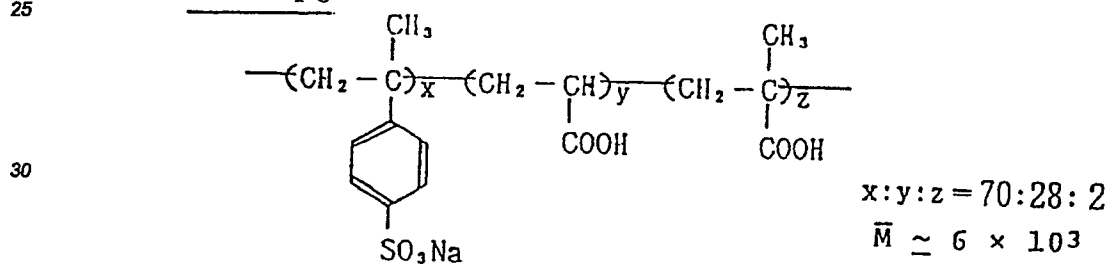
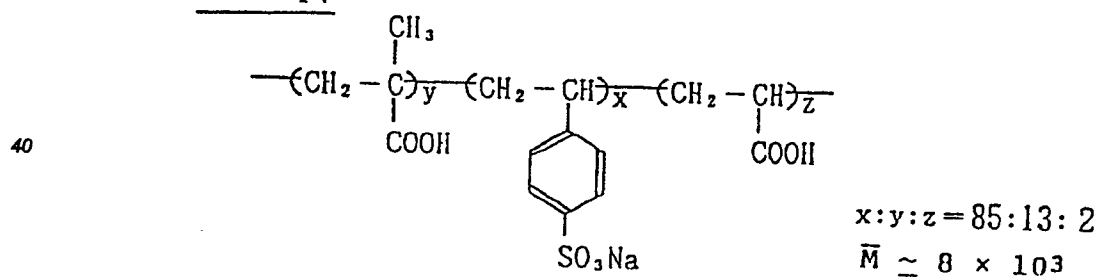
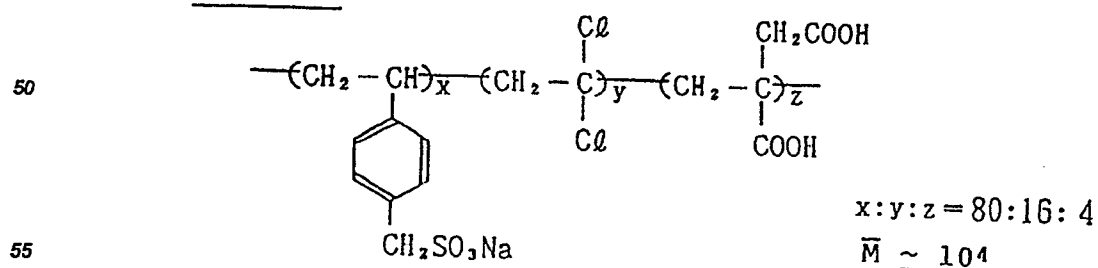
$$\bar{M} \approx 5 \times 10^3$$

A - 13

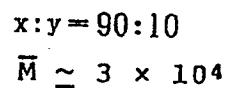


$$x:y = 60:40$$

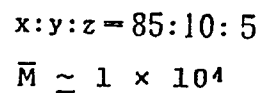
$$M_n = 8 \times 10^3$$

A - 14A - 15A - 16A - 17A - 18

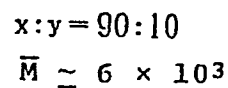
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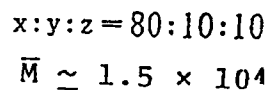
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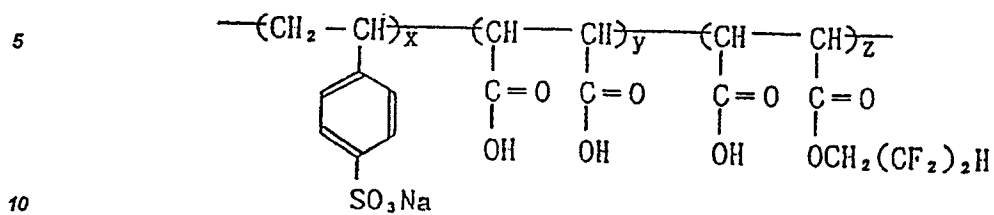


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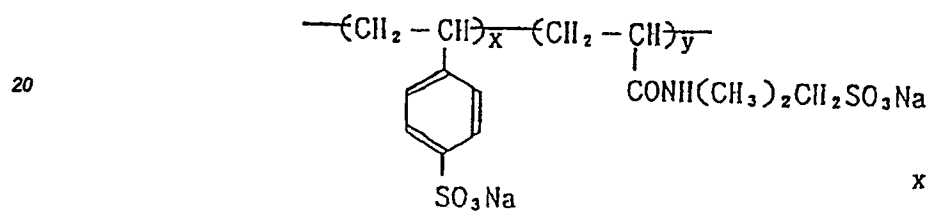
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A - 24

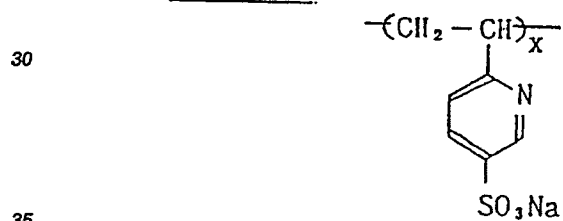
$$x:y:z = 50:40:10$$

$$\bar{M} \simeq 10^5$$

A - 25

$$x:y = 80:20$$

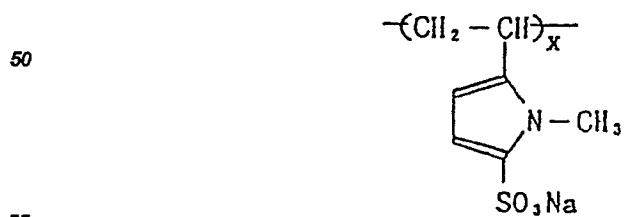
$$\bar{M} \simeq 5 \times 10^4$$

A - 26

$$\bar{M} \simeq 10^5$$

A - 27

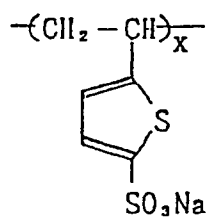
$$\bar{M} \simeq 2 \times 10^4$$

A - 28

$$\bar{M} \simeq 2 \times 10^4$$

A - 29

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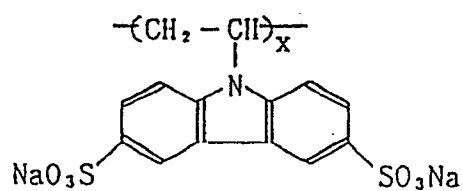


$$\bar{M} \simeq 1.5 \times 10^5$$

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A - 30

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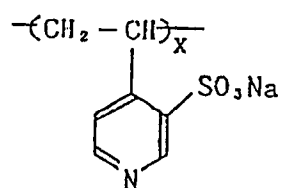


$$\bar{M} \simeq 3 \times 10^5$$

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A - 31

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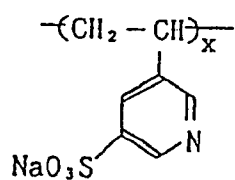


$$\bar{M} \simeq 2.8 \times 10^5$$

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A - 32

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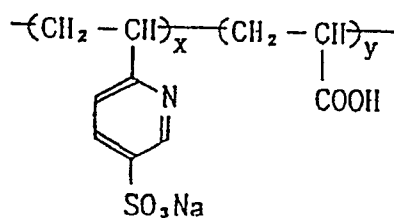


$$\bar{M} \simeq 5 \times 10^4$$

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A - 33

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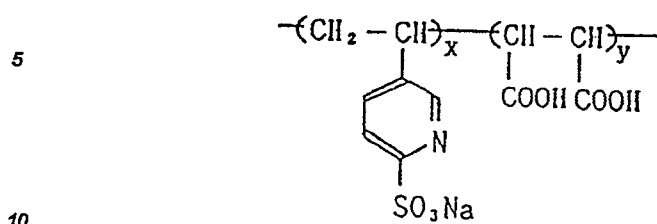


$$x : y = 60 : 40$$

$$\bar{M} \simeq 8 \times 10^4$$

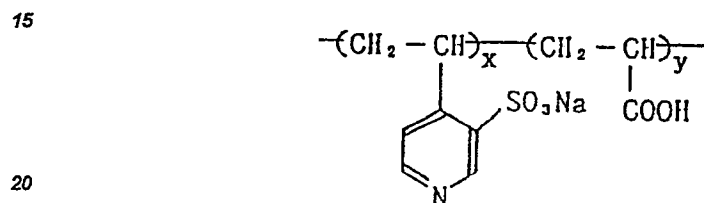
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A - 34

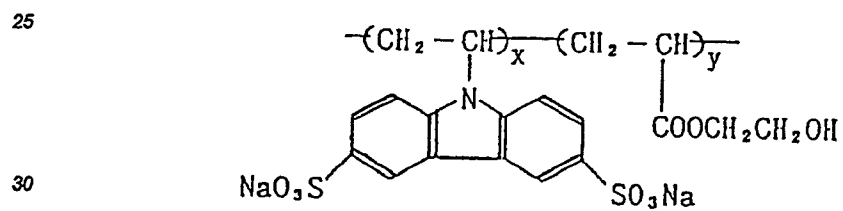
$$x : y = 70 : 30$$

$$\bar{M} \simeq 5 \times 10^3$$

A - 35

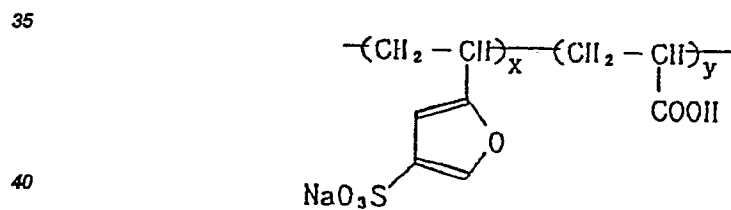
$$x : y = 80 : 20$$

$$\bar{M} \simeq 5 \times 10^4$$

A - 36

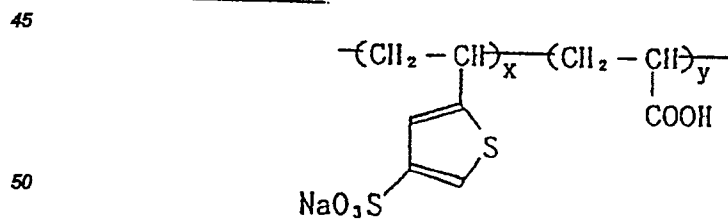
$$x : y = 75 : 25$$

$$\bar{M} \simeq 4 \times 10^4$$

A - 37

$$x : y = 80 : 20$$

$$\bar{M} \simeq 6 \times 10^4$$

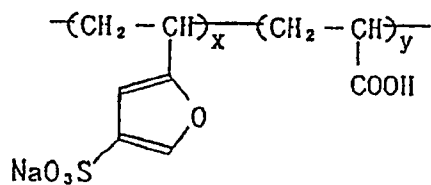
A - 38

$$x : y = 90 : 10$$

$$\bar{M} \simeq 4 \times 10^4$$

A - 39

5



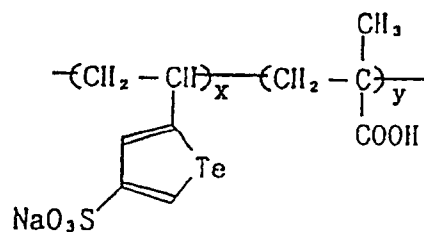
$$x : y = 55 : 45$$

$$\bar{M} \approx 2 \times 10^4$$

10

A - 40

15



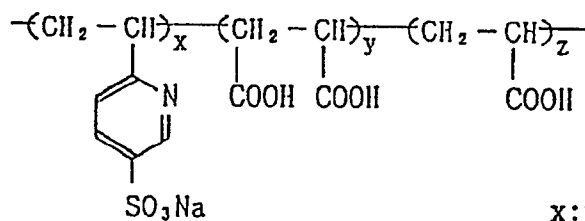
$$x : y = 90 : 10$$

$$\bar{M} \approx 6 \times 10^4$$

20

A - 41

25



$$x : y : z = 80 : 10 : 10$$

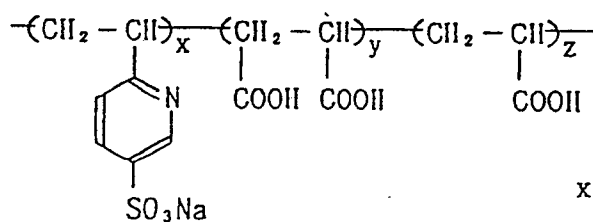
$$\bar{M} \approx 10^4$$

30

35

A - 42

40



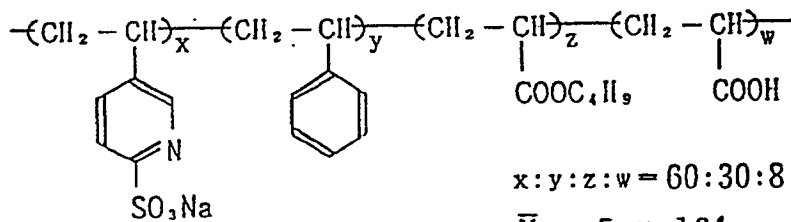
$$x : y : z = 70 : 25 : 5$$

$$\bar{M} \approx 3 \times 10^4$$

45

A - 43

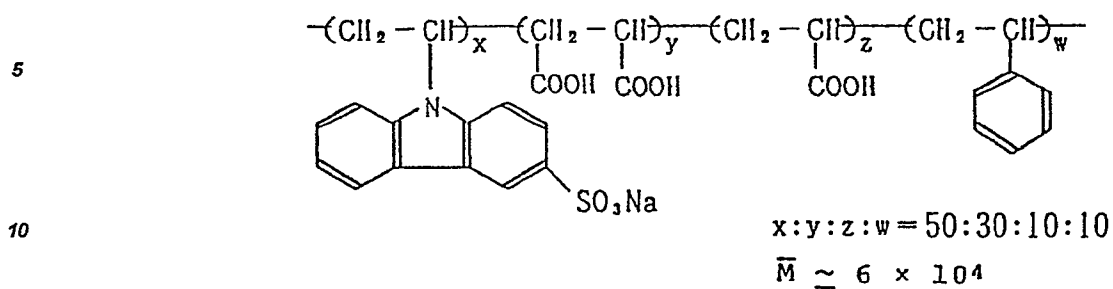
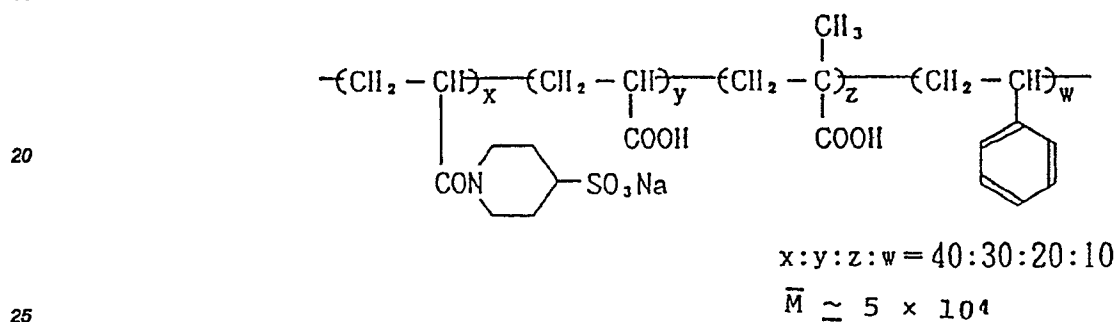
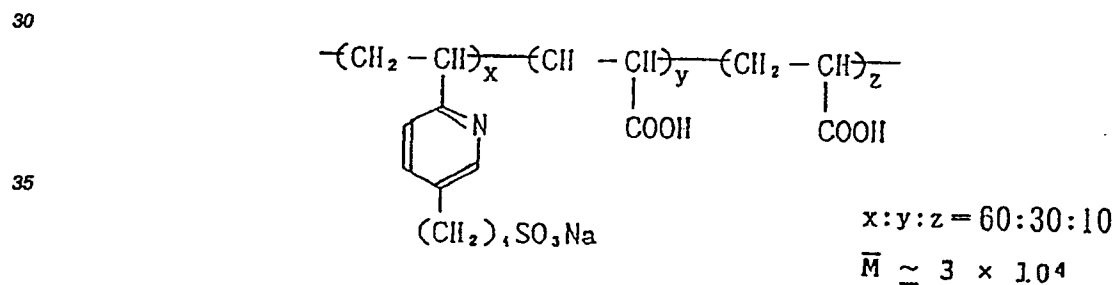
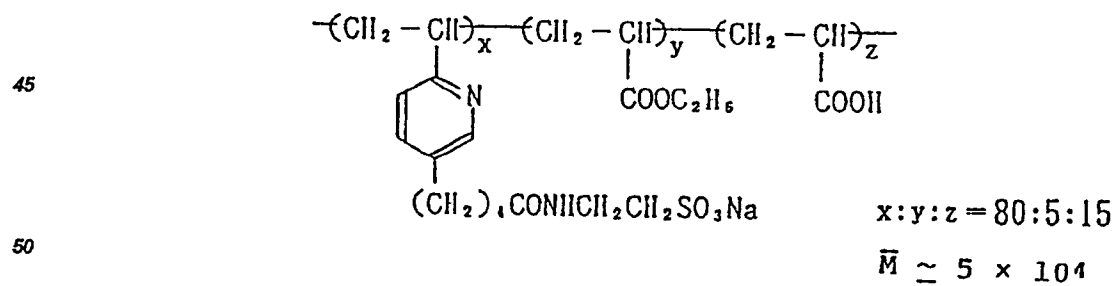
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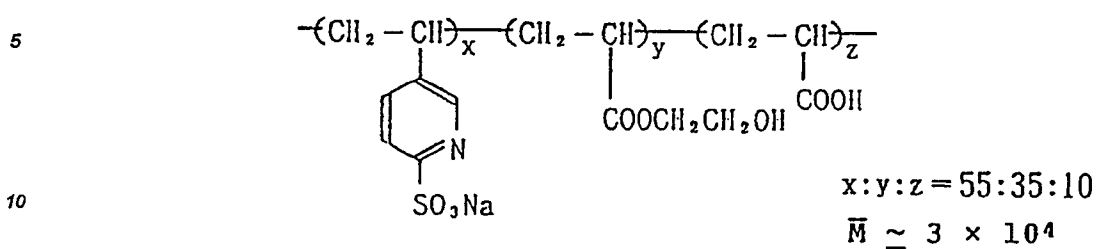
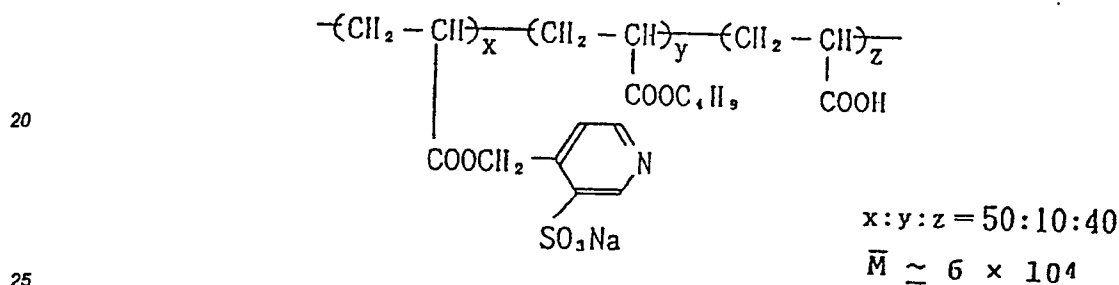
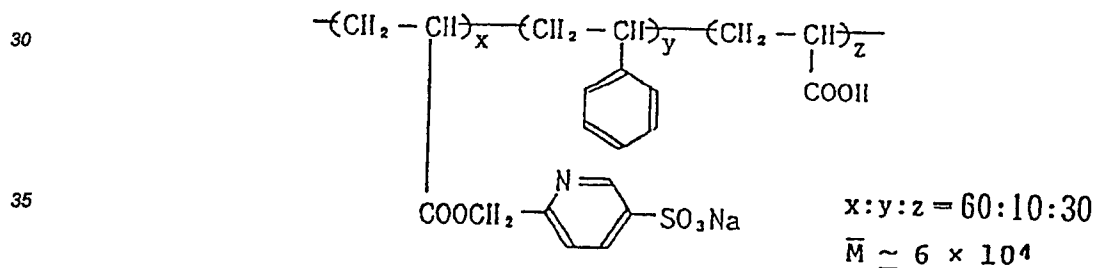


$$x : y : z : w = 60 : 30 : 8 : 2$$

$$\bar{M} \approx 5 \times 10^4$$

55

A - 44A - 45A - 46A - 47

A - 48A - 49A - 50

40 In the compounds A-1 to A-50, x, y and z represent the amounts of respective components in mole percent, and $\bar{M}$ represents the average molecular weight (more specifically, number average molecular weight) as measured by GPC and expressed in terms of polyethylene glycol.

The polymers listed above can be synthesized by polymerizing monomers that are either commercially available or prepared in the usual manner. These polymers are preferably added in amounts of 0.01 - 10 g/m², more preferably 0.1 - 5 g/m².

45 The hydrophobic polymer latex that may be contained in the antistatic layer is composed of so-called "latex particles" that are substantially insoluble in water. This hydrophobic polymer is obtained by polymerizing any combinations of monomers as selected from among styrene, styrene derivatives, alkyl acrylates, alkyl methacrylates, olefin derivatives, halogenated ethylene derivatives, vinyl ester derivatives, acrylonitrile, etc.

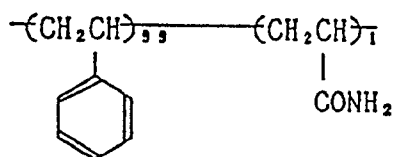
50 A latex can be made from the hydrophobic polymer by either one of the following two methods: emulsion polymerization; and dissolving a solid polymer in a low-boiling solvent to form a dispersion in which it is finely dispersed and thereafter the solvent is distilled off. Emulsion polymerization is preferred since it yields a latex comprised of fine and uniformly sized particles.

The hydrophobic polymer will achieve its intended function if it has a molecular weight of at least 3,000 and the transparency of the antistatic layer is substantially independent of the molecular weight of that polymer.

55 Specific examples of the hydrophobic polymer latex that can be used in the present invention are listed below.

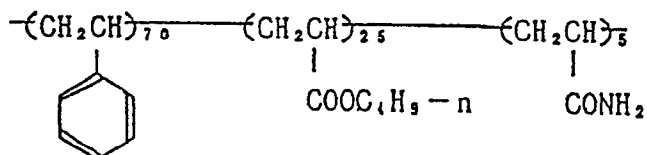
B - 1

5



B - 2

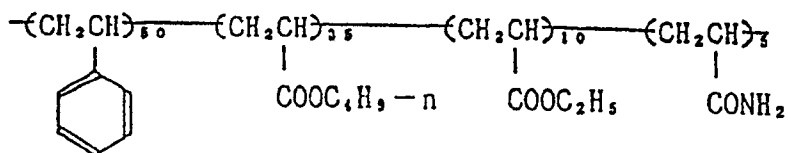
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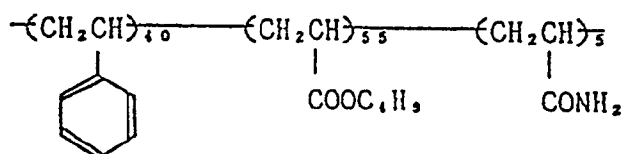
B - 3

20



B - 4

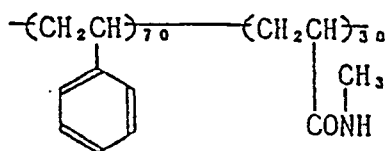
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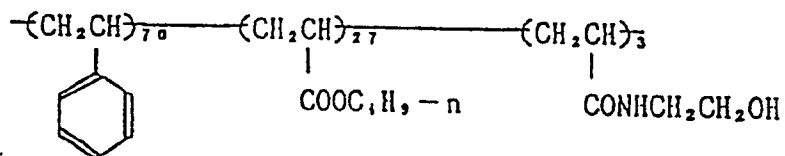
B - 5

35



B - 6

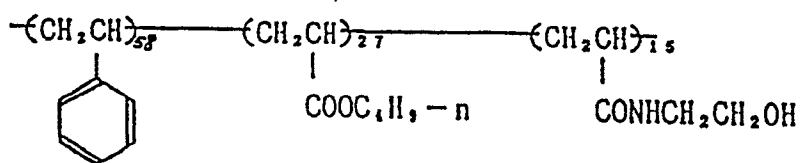
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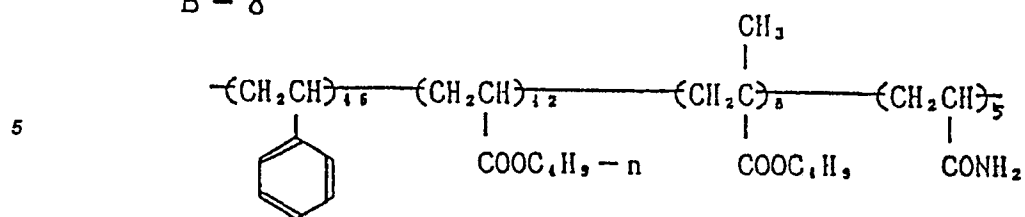
B - 7

50

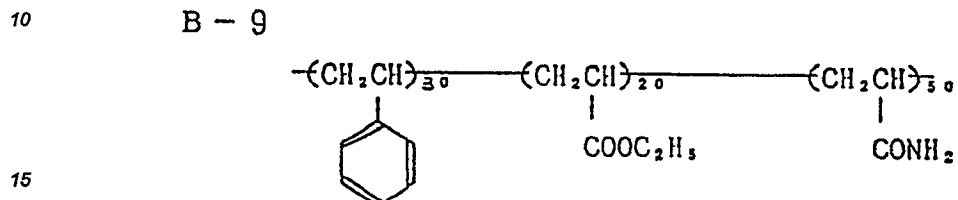


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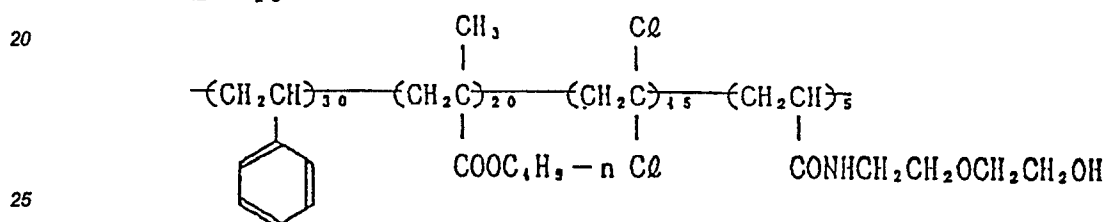
B - 8



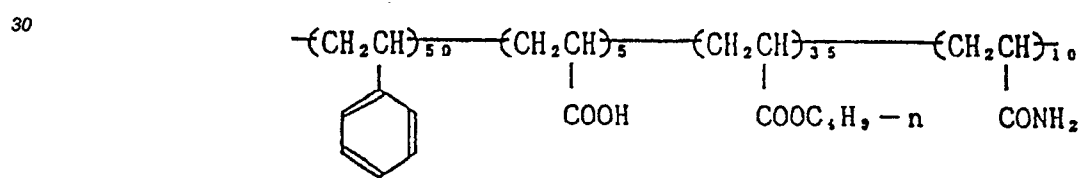
B - 9



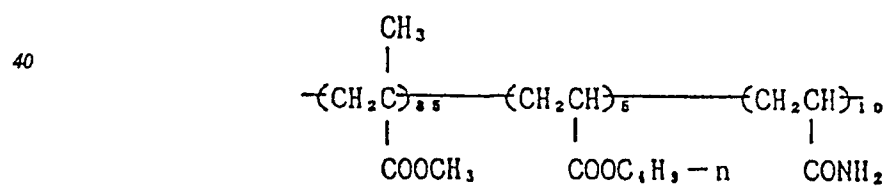
B - 10



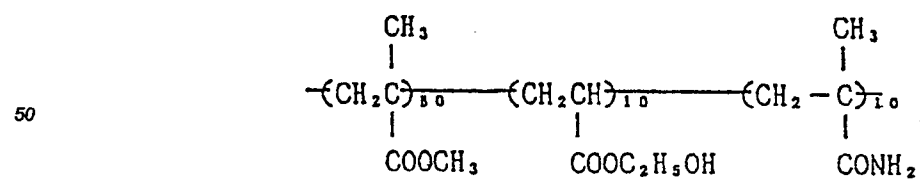
B - 11



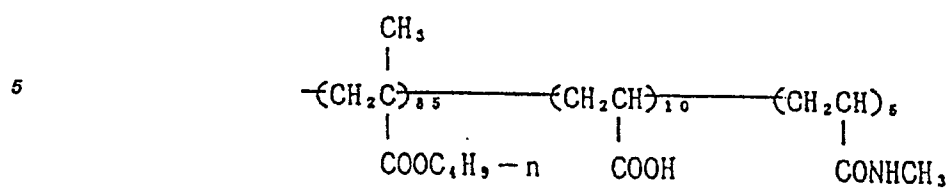
B - 12



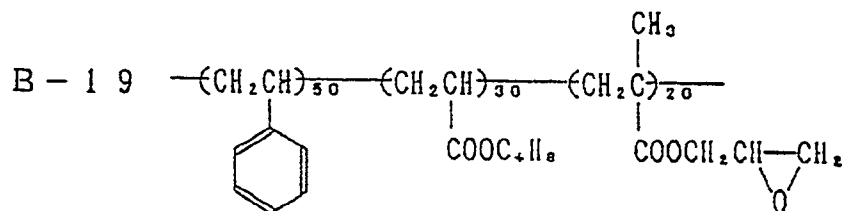
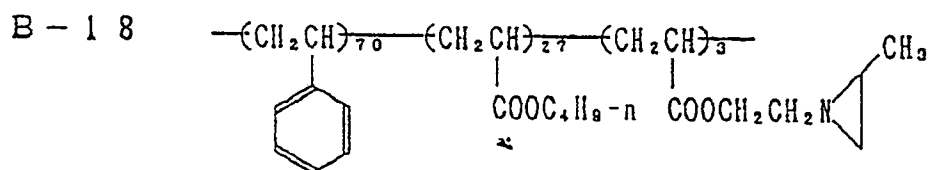
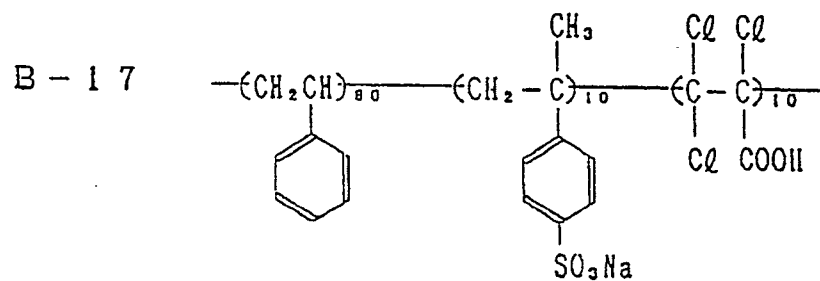
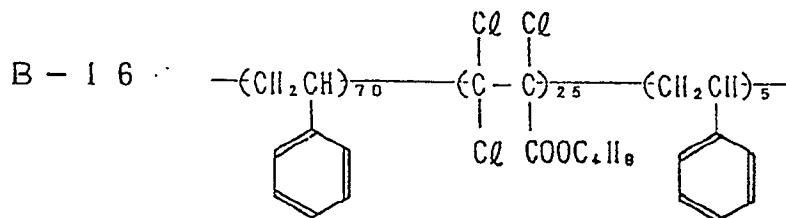
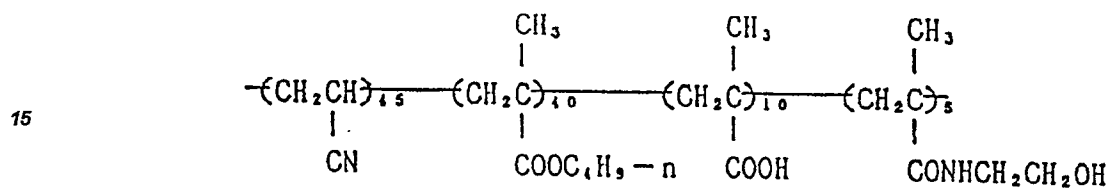
B - 13

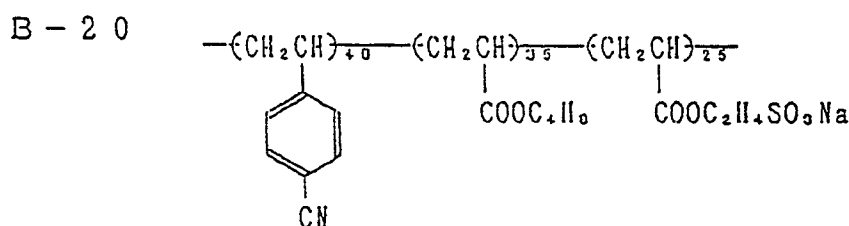


B - 14



B - 15





These hydrophobic polymer latices may be used either on their own or as admixtures. They are preferably added in amounts of 0.01 - 10 g/m², more preferably 0.1 - 1 g/m².

The antistatic layer may be located closer to a transparent support than light-sensitive silver halide emulsion layers (which are hereinafter sometimes referred to as "light-sensitive layers"); alternatively, the antistatic layer may be located on the back side of the support, or on the side opposite the light-sensitive layers.

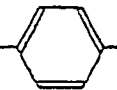
The antistatic layer described above is formed on a transparent support by coating procedures. All kinds of photographic transparent substrates can be used but polyethylene terephthalate or cellulose triacetate films that transmit at least 90% of visible light are preferred. Such transparent supports are prepared by methods that are well known to one skilled in the art; if desired, they may be blued by adding dyes in small amounts that do substantially no harm to light transmission. After corona discharge treatment, the supports may be coated with a subbing layer that contains a latex polymer. Corona discharge is preferably applied with an energy of 1 mW - 1 kW/m² per min. In a particularly preferred embodiment, the support subbed with a latex layer is subjected to a second corona discharge treatment before the antistatic layer is applied.

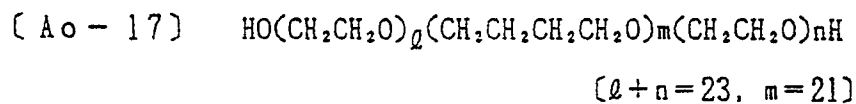
Polyfunctional aziridine compounds are preferably used to cure the antistatic layer. Particularly preferred are bi- or trifunctional aziridine compounds having a molecular weight of no more than 600.

Nonionic surfactants may be used either as surfactants during emulsion polymerization for the preparation of the hydrophobic polymer latex or as dispersants in the dispersion method described above. Polyalkylene oxide compounds are preferable used. Polyalkylene oxide compounds are those compounds which contain at least 3 but no more than 500 polyalkylene oxide chains in the molecule. Such polyalkylene oxide compounds can be synthesized by the condensation reaction between polyalkylene oxides and compounds having an active hydrogen atom such as aliphatic alcohols, phenols, aliphatic acids, aliphatic mercaptans or organic amines, or by condensing polyols such as polypropylene glycol or polyoxytetramethylene polymers with aliphatic mercaptans, organic amines, ethylene oxide or propylene oxide. The polyalkylene oxide compounds need not contain only one polyalkylene oxide chain in the molecule but they may contain two or more segments of a block copolymer as the polyalkylene oxide chain. In this case, the total degree of polymerization of polyalkylene oxide segments is preferably in the range of 3 - 100.

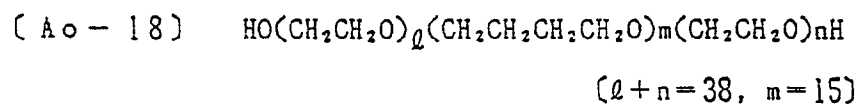
Specific but non-limiting examples of the polyalkylene oxide compounds that can be used in the present invention are listed below.

Exemplary compounds

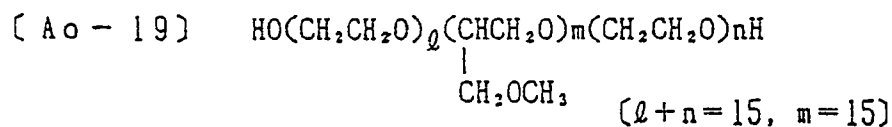
5	[A o - 1]	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	$(n=4)$
	[A o - 2]	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	$(n=35)$
10	[A o - 3]	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	$(n=135)$
	[A o - 4]	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	$(n=225)$
15	[A o - 5]	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	$(n=450)$
	[A o - 6]	$n\text{-C}_4\text{H}_9\text{O}(\text{CH}_2\text{CH}_2\text{O})_\ell\text{H}$	$(\ell=20)$
20	[A o - 7]	$n\text{-C}_8\text{H}_{17}\text{O}(\text{CH}_2\text{CH}_2\text{O})_\ell\text{H}$	$(\ell=30)$
	[A o - 8]	$n\text{-C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_\ell\text{H}$	$(\ell=30)$
25	[A o - 9]	$n\text{-C}_9\text{H}_{19}$  $\text{O}(\text{CH}_2\text{CH}_2\text{O})_\ell\text{H}$	$(\ell=30)$
30	[A o - 10]	$n\text{-C}_{12}\text{H}_{25}\text{S}(\text{CH}_2\text{CH}_2\text{O})_\ell\text{H}$	$(\ell=30)$
	[A o - 11]	$\text{C}_4\text{H}_9\text{S}(\text{CH}_2\text{CH}_2\text{O})_n\text{COCH}_2\text{CH}_2\text{COOH}$	$(n=50)$
35	[A o - 12]	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_\ell(\text{CH}_2)_m(\text{CH}_2\text{CH}_2\text{O})_n\text{COCH}_2\text{CH}_2\text{COOH}$	$(\ell+n=70, m=5)$
40	[A o - 13]	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_\ell(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	$(\ell+n=15, m=17)$
45	[A o - 14]	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_\ell(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	$(\ell+n=30, m=35)$
50	[A o - 15]	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_\ell(\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	$(\ell+n=15, m=15)$
55	[A o - 16]	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_\ell(\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	$(\ell+n=30, m=15)$



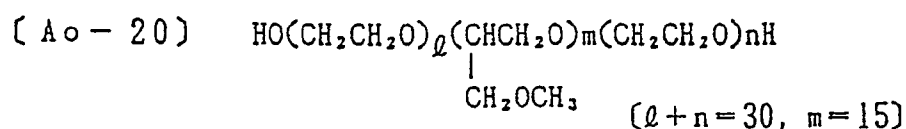
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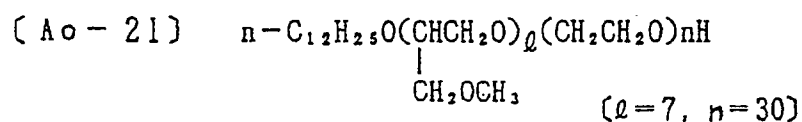
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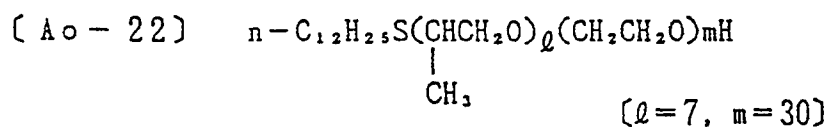
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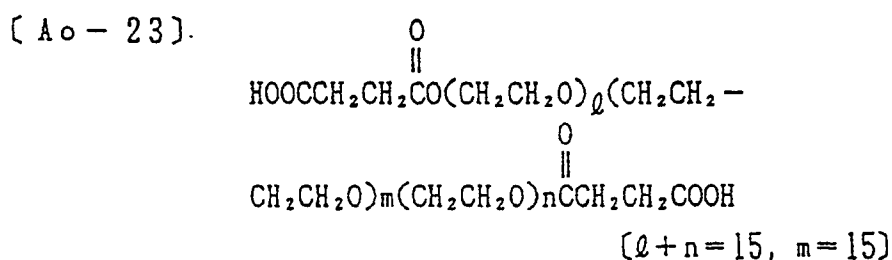
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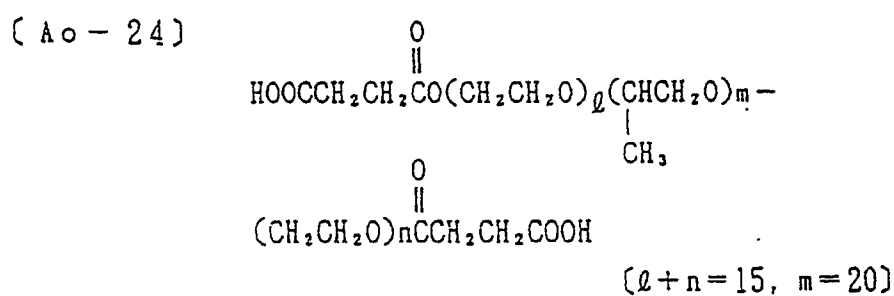


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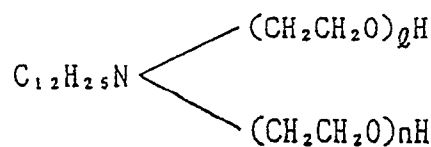


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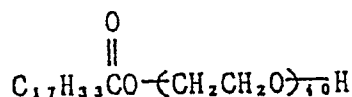
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[A o - 25]

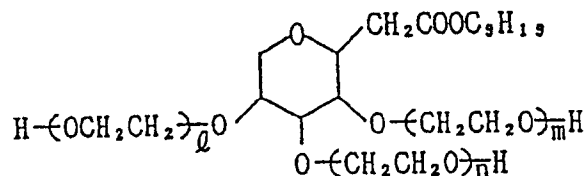


$$(\ell + n = 30)$$

[A o - 26]

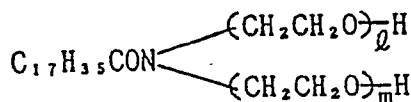


[A o - 27]



$$\ell + m + n = 20$$

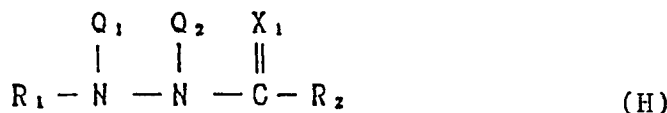
[A o - 28]



$$\ell + m = 12$$

The antistatic layer on the support is overlaid with at least one light-sensitive silver halide emulsion layer. It is preferred for the purposes of the present invention that a hydrazine compound is contained in one or more light-sensitive silver halide emulsion layers.

The hydrazine compounds to be preferably used in the present invention are represented by the following general formula (H):



where R_1 is a monovalent organic residue; R_2 is a hydrogen atom or a monovalent organic residue; Q_1 and Q_2 are each a hydrogen atom, an optionally substituted alkylsulfonyl group, or an optionally substituted arylsulfonyl group; X_1 is an oxygen atom or a sulfur atom.

Among the compounds represented by the general formula (H), one in which X_1 is an oxygen atom and X_2 is a hydrogen atom is particularly preferred.

Monovalent organic groups represented by R_1 and R_2 include aromatic residues, heterocyclic residues and aliphatic residues.

Illustrative aromatic residues include a phenyl group and a naphthyl group, which may have such substituents as alkyl, alkoxy, acylhydrazino, dialkylamino, alkoxy carbonyl, cyano, carboxyl, nitro, alkylthio, hydroxyl, sulfonyl, carbamoyl, halogen, acylamino, sulfonamido, urea and thiourea. Substituted phenyl groups include 4-methylphenyl, 4-ethylphenyl, 4-oxyethylphenyl, 4-dodecylphenyl, 4-carboxyphenyl, 4-diethylaminophenyl, 4-octylaminophenyl, 4-benzylaminophenyl, 4-acetamido-2-methylphenyl, 4-(3-ethylthioureido)phenyl, 4-[2-(2,4-

di-tert-butylphenoxy)butylamido]phenyl and 1,1-dibenzylsemicarbazide.

Illustrative heterocyclic residues are 5- or 6-membered single or fused rings having at least one of oxygen, nitrogen, sulfur and selenium atoms. These rings may have substituents. Specific examples of heterocyclic residues include: pyrroline, pyridine, quinoline, indole, oxazole, benzoxazole, naphthoxazole, imidazole, benzimidazole, thiazoline, thiazole, benzothiazole, naphthothiazole, selenazole, benzoselenazole and naphthoselenazole rings.

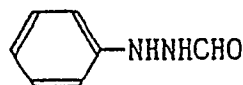
These hetero rings may be substituted by alkyl groups having 1 - 4 carbon atoms such as methyl and ethyl, alkoxy groups having 1 - 4 carbon atoms such as methoxy and ethoxy, aryl groups having 6 - 18 carbon atoms such as phenyl, halogen atoms such as chlorine and bromine, alkoxy carbonyl groups, cyano group, amido group, etc.

Illustrative aliphatic residues include straightchained or branched alkyl groups, cycloalkyl groups, substituted alkyl or cycloalkyl groups, alkenyl groups and alkynyl groups. Exemplary straight-chained or branched alkyl groups are alkyl groups having 1 - 18, preferably 1 - 8, carbon atoms, such as methyl, ethyl, isobutyl and 1-octyl. Exemplary cycloalkyl groups include those having 3-10 carbon atoms, such as cyclopropyl, cyclohexyl, adamantyl, etc. Substituents on alkyl and cycloalkyl groups include an alkoxy group (e.g. methoxy, ethoxy, propoxy or butoxy), an alkoxy carbonyl group, a carbamoyl group, a hydroxyl group, an alkylthio group, an amido group, an acyloxy group, a cyano group, a sulfonyl group, a halogen atom (e.g. Cl, Br, F or I), an aryl group (e.g. phenyl, halogen-substituted phenyl or alkyl-substituted phenyl), etc. Specific examples of substituted cycloalkyl group and substituted alkyl group include 3-methoxypropyl, ethoxycarbonylmethyl, 4-chlorocyclohexyl, benzyl, p-methylbenzyl and p-chlorobenzyl. An exemplary alkenyl group is an allyl group, and an exemplary alkynyl group is a propargyl group.

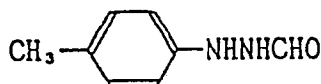
Preferred examples of the hydrazine compound that can be used in the present invention are listed below and it should be understood that they are by no means intended to limit the scope of the present invention.

Exemplary compounds

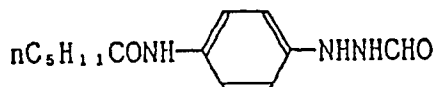
H - 1



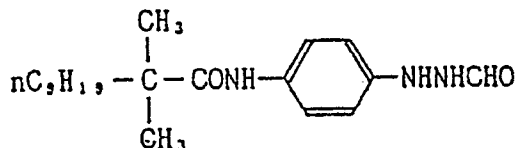
H - 2



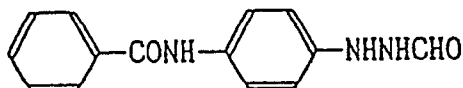
H - 3



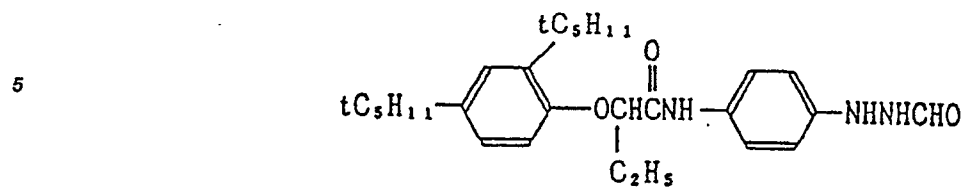
H - 4



H - 5

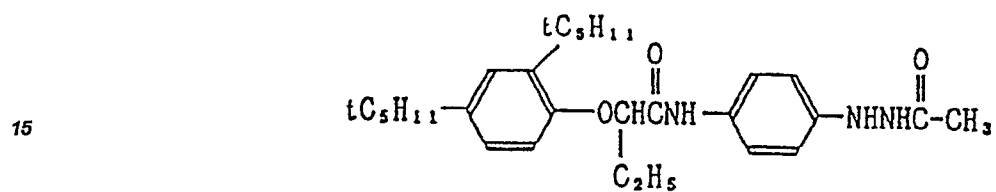


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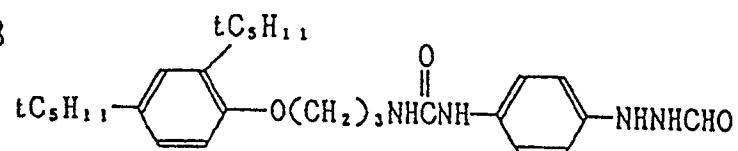
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H - 7



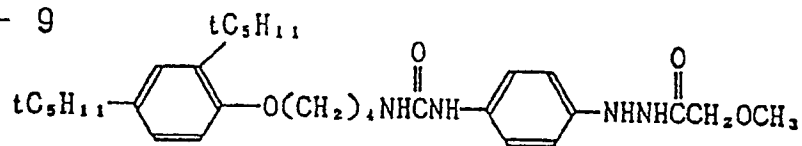
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H - 8



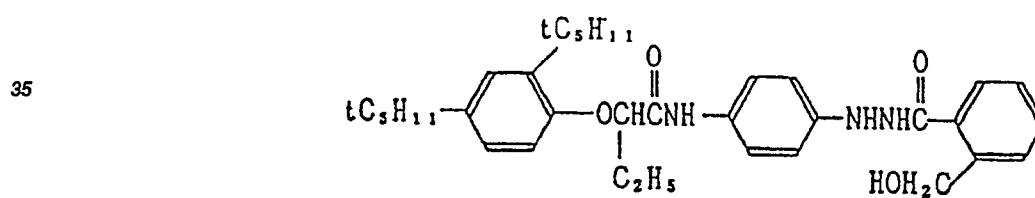
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H - 9



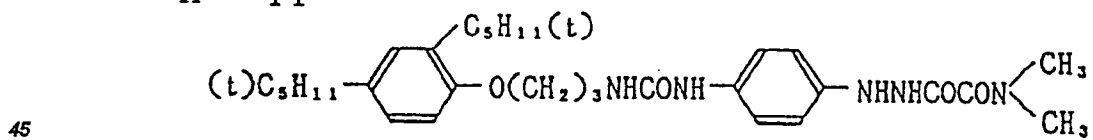
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H - 10

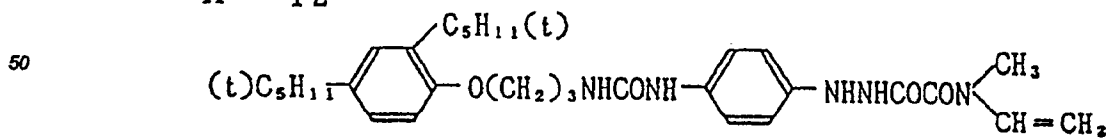


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H - 11

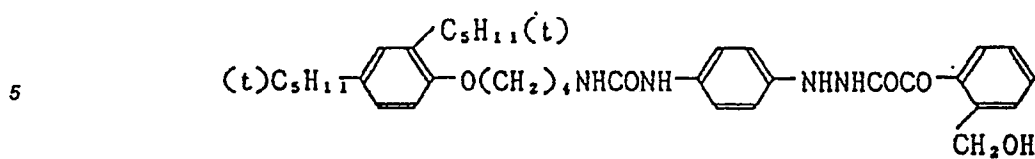


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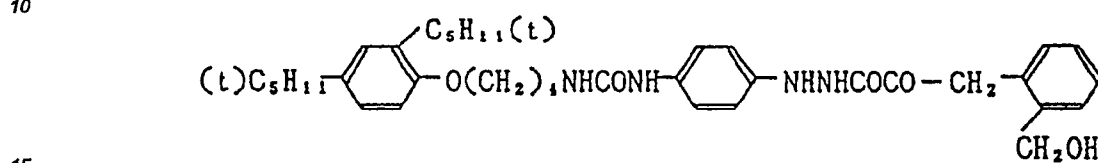


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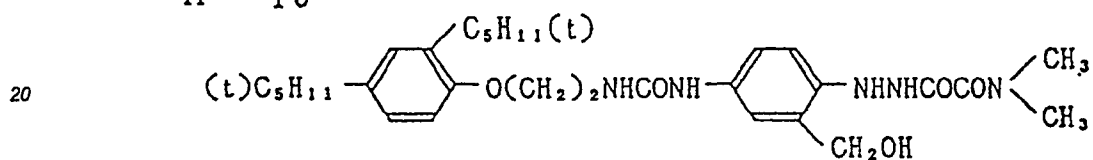
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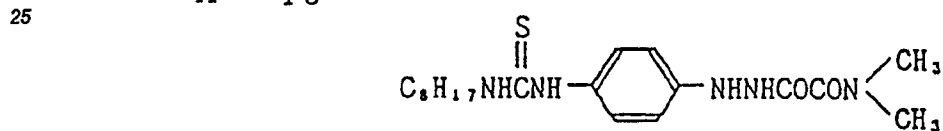
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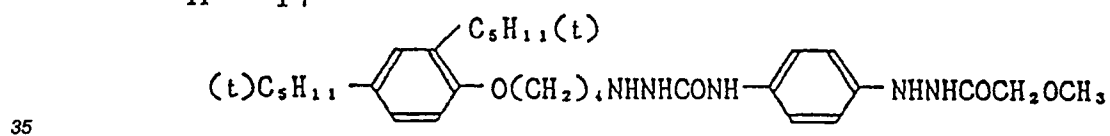
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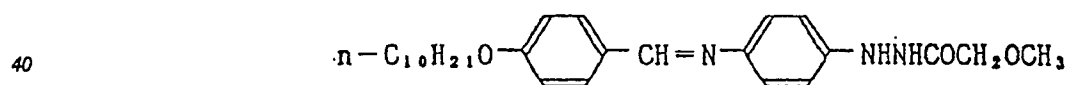
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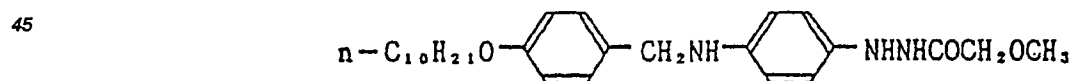
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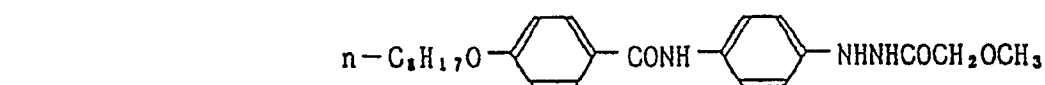
H - 18



H - 19

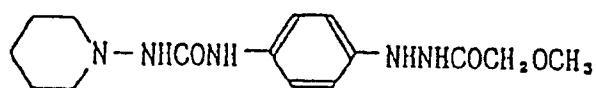


H - 20



H - 21

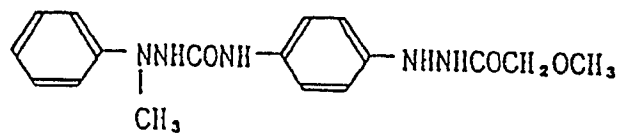
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H - 22

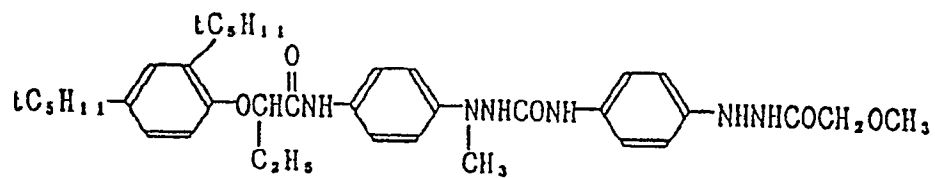
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H - 23

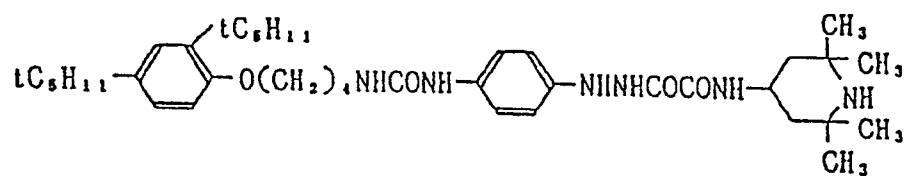
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H - 24

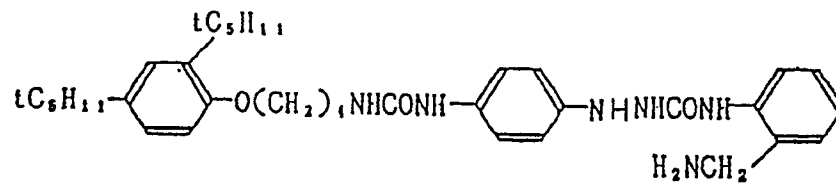
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H - 25

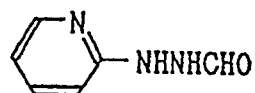
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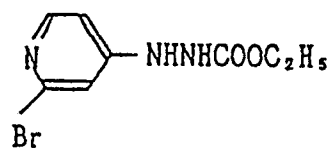
H - 26

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H - 27

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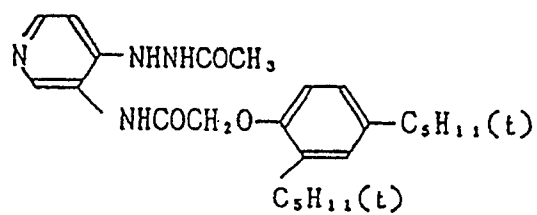


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H - 28

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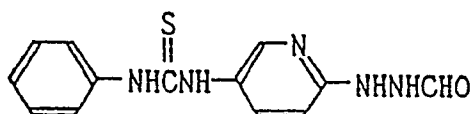
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H - 29

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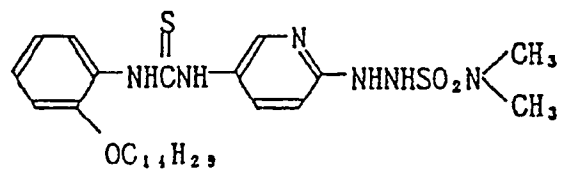
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H - 30

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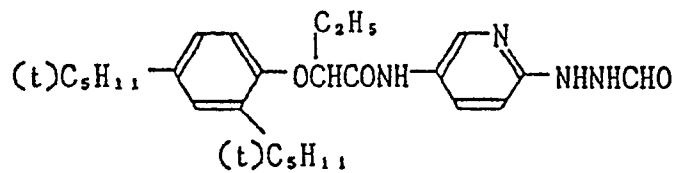
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H - 31

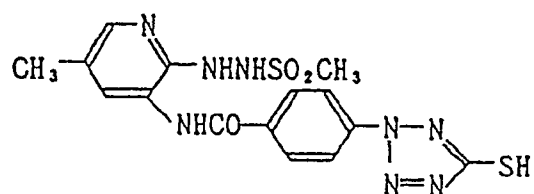
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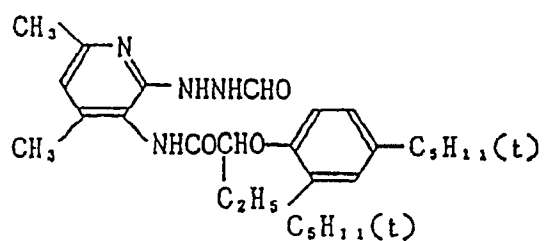


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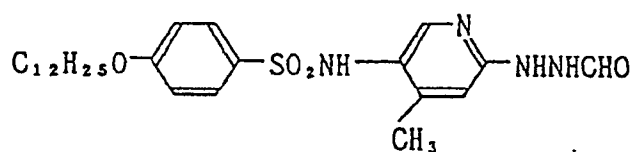
H - 32



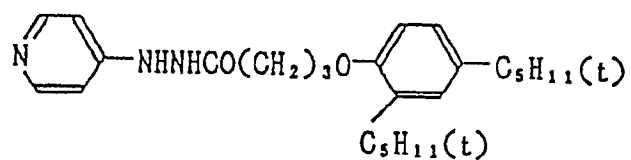
H - 33



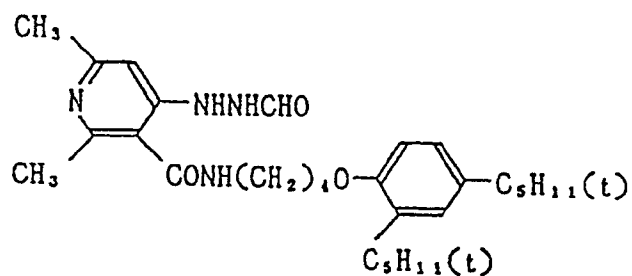
H - 34



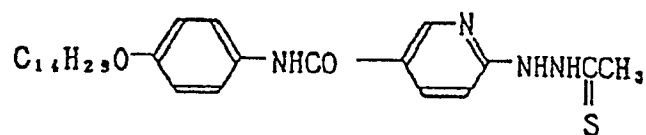
H - 35



H - 36

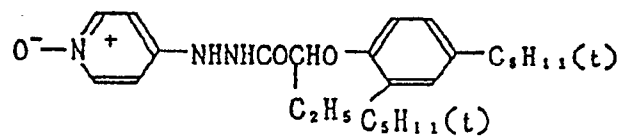


H - 37



H - 38

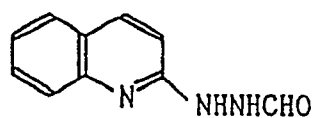
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H - 39

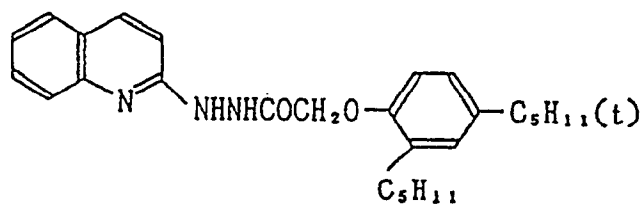
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H - 40

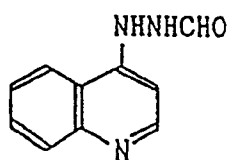
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H - 41

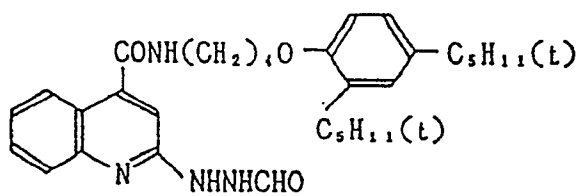
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H - 42

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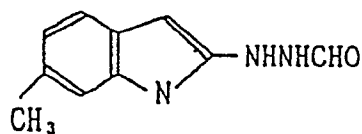


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H - 43

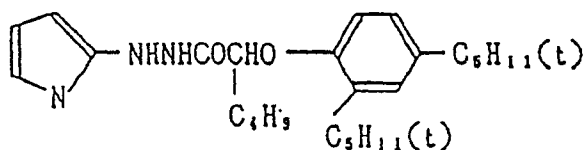
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H - 44

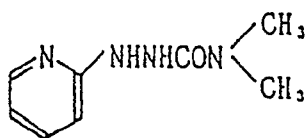
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H - 45

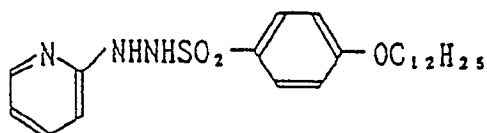
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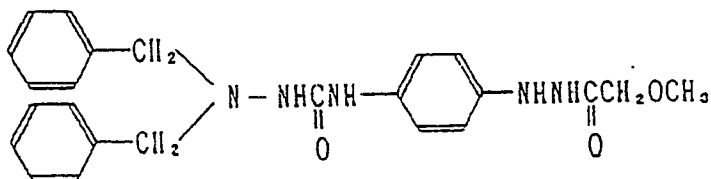
H - 46

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H - 47

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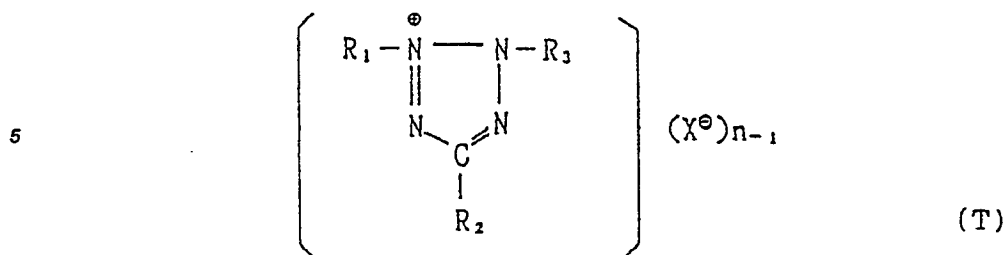
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The hydrazine compounds of the general formula (H) are incorporated in a silver halide emulsion layer and/or in a non-light-sensitive layer that is on the same side of a support as where a silver halide emulsion layer is present. Preferably, the hydrazine compounds are incorporated in a silver halide emulsion layer and/or an underlying layer. The hydrazine compounds are preferably added in amounts of 10^{-5} - 10^{-1} mole per mole of silver, more preferably 10^{-4} - 10^{-2} mole per mole of silver.

50

It is also preferred for the purposes of the present invention that a tetrazolium compound is contained in one or more light-sensitive silver halide emulsion layers. The tetrazolium compounds that can be used in the present invention are represented by the following general formula (T):

55



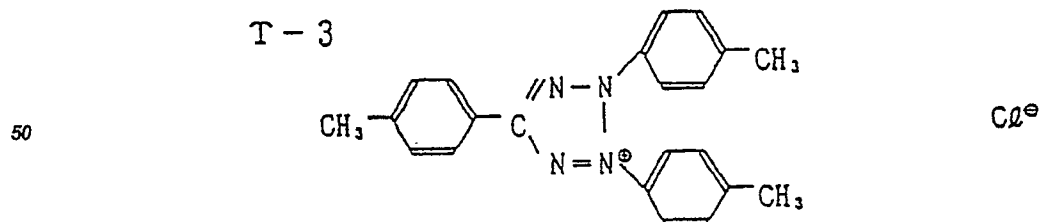
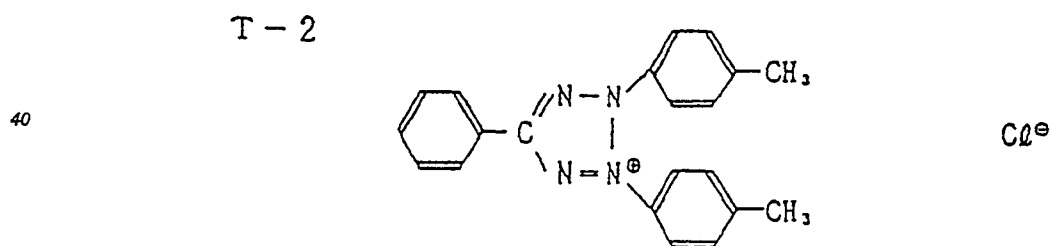
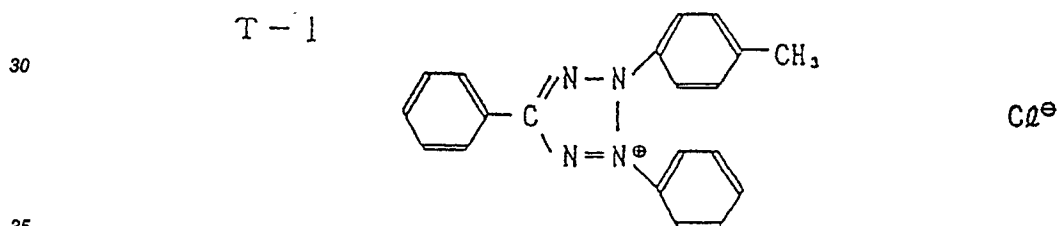
where R_1 , R_2 and R_3 are each a substituted or unsubstituted phenyl group; and $X^\ominus$ is an anion.

The phenyl group in the triphenyltetrazolium compound represented by the general formula (T) may have a substituent which is preferably a hydrogen atom or a group having a negative or positive Hammett's sigma value (δP) which is a measure of electron withdrawing property, with groups having a negative of being particularly preferred.

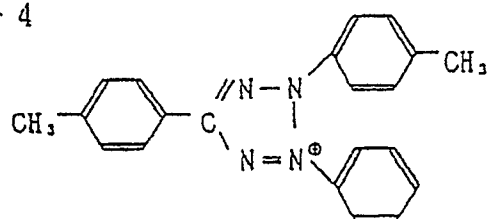
Discussions of the Hammett's sigma value of substituents in the phenyl group are found in the report of C. Hansch et al., Journal of Medical Chemistry, Vol. 20, p. 304, 1977 and in many other papers. Examples of particularly preferred groups having a negative sigma value include: methyl ($\delta P = -0.17$; all parenthesized values that follow refer to δP); ethyl (-0.15); cyclopropyl (-0.21); n-propyl (-0.13); iso-propyl (-0.15); cyclobutyl (-0.15); n-butyl (-0.16); iso-butyl (-0.20); n-pentyl (-0.15); cyclohexyl (-0.22); amino (-0.66); acetylamino (-0.15); hydroxyl (-0.37); methoxy (-0.27); ethoxy (-0.24); propoxy (-0.25); butoxy (-0.32); and pentoxy (-0.34). These groups are all useful as substituents in the compounds of the general formula (T).

Specific but non-limiting examples of the compounds of the general formula (T) that can be used in the present invention are listed below.

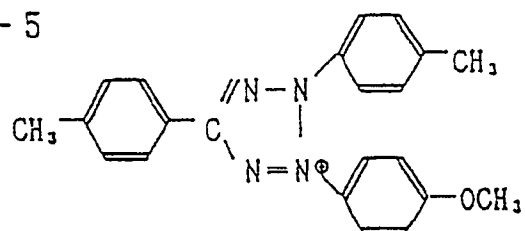
25
Exemplary compounds



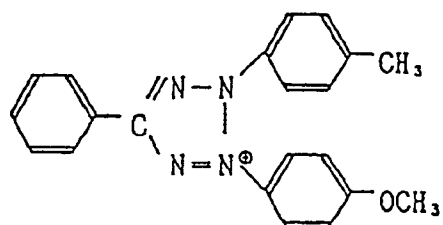
T - 4

Cl[⊖]

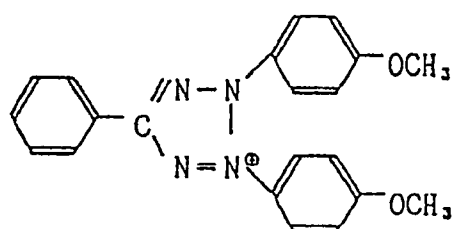
T - 5

Cl[⊖]

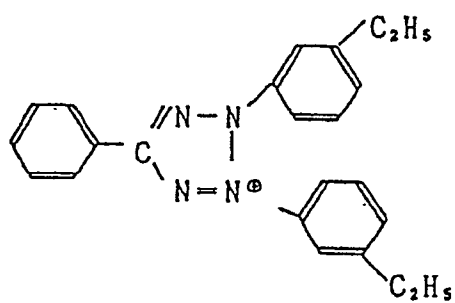
T - 6

Cl[⊖]

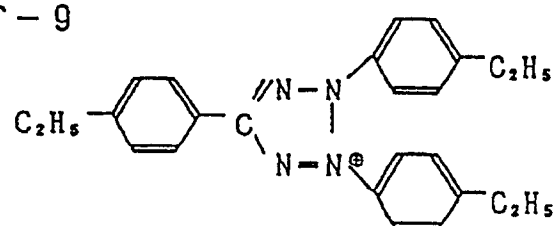
T - 7

Cl[⊖]

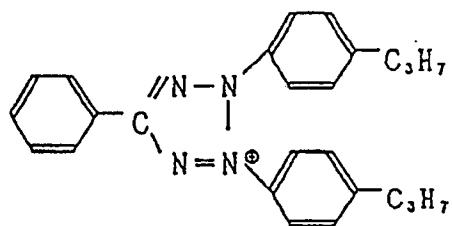
T - 8

Cl[⊖]

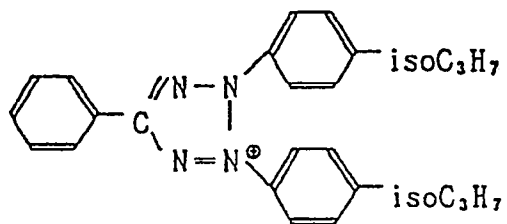
T - 9

Cl[⊖]

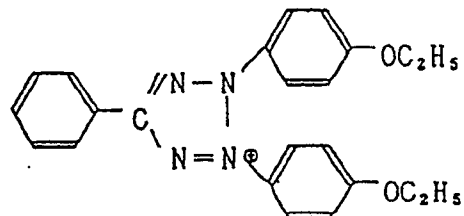
T-10

 $\text{Cl}^\ominus$

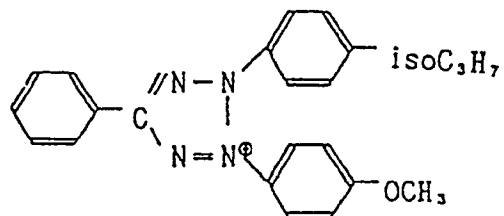
T-11

 $\text{Cl}^\ominus$

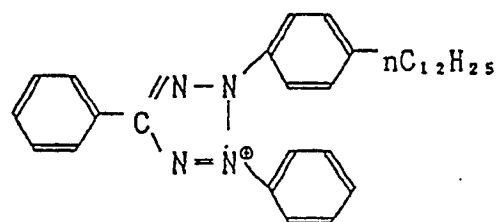
T-12

 $\text{Cl}^\ominus$

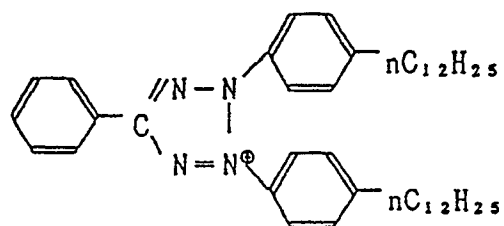
T-13

 $\text{Cl}^\ominus$

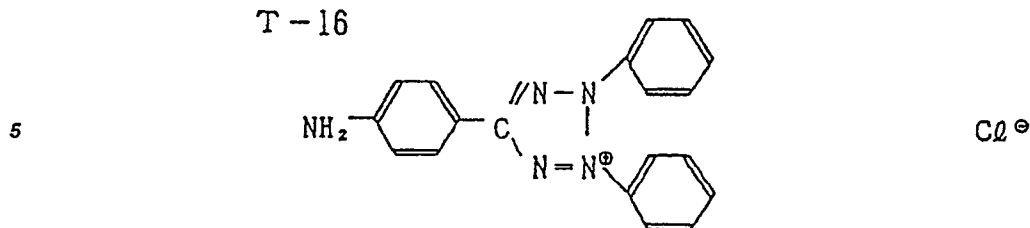
T-14

 $\text{Cl}^\ominus$

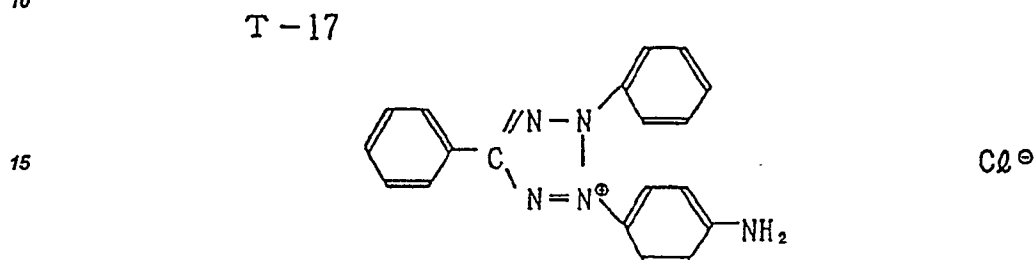
T-15

 $\text{Cl}^\ominus$

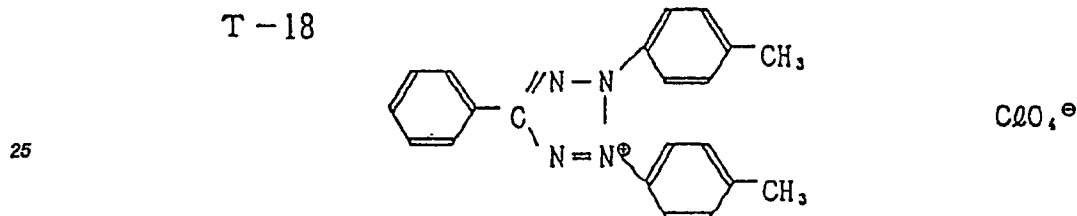
T - 16



T - 17



T - 18



30 The tetrazolium compounds to be used in the present invention can be easily synthesized by known methods, for example, the one described in Chemical Reviews, 55, 335-483.

The tetrazolium compounds represented by the general formula (T) are preferably used in amounts ranging from about 1 mg to 10 g, more preferably from about 10 mg to about 2 g, per mole of the silver halide contained in the silver halide photographic material.

35 The silver halide emulsion to be used in the light-sensitive material of the present invention may incorporate any types of silver halides such as silver bromide, silver chloride, silver iodobromide, silver chlorobromide and silver chloriodobromide that are commonly employed in silver halide emulsions. Silver halide grains may be prepared by any of the acid, neutral and ammoniacal methods.

40 Silver halide grains may have a uniform distribution of silver halide composition in their interior or they may be core/shell grains having different silver halide compositions in the interior and the surface layer. The grains may be of such a type that a latent image is predominantly formed on the surface or they may be of a type that forms a latent image predominantly in the interior.

45 The silver halide emulsions to be used in the present invention may be stabilized with various compounds such as those described in U.S. Patent Nos. 2,444,607, 2,716,062, 3,512,982, West German Patent Publication Nos. 1,189,380, 2,058,626, 2,118,411, JP-B-47-4417, West German Patent Publication No. 2,149,789, as well as JP-B-39-2825 and 49-13566. Preferred examples of such compounds include: pyrimidine compounds such as 5,6-trimethylene-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, and 5-methyl-6-bromo-7-hydroxy-S-triazolo(1,5-a)pyrimidine; gallic acid esters or salts such as isoamyl gallate, dodecyl gallate, propyl gallate and sodium gallate; mercaptans such as 1-phenyl-5-mercaptotetrazole and 2-mercaptobenzothiazole; benzotriazoles such as 5-bromobenzotriazole and 5-methylbenzotriazole; and benzimidazoles such as 6-nitrobenzimidazole.

50 An amino compound may be incorporated in the light-sensitive material of the present invention and/or in a developing solution used for its development.

55 For enhanced developability, developing agents such as Phenidone and hydroquinone, or restrainers such as benzotriazole may be incorporated in emulsion layers. Alternatively, such developing agents or restrainers may be incorporated in the backing layer in order to improve the ability of processing solutions.

Gelatin is a hydrophilic colloid that can be used with particular advantage in the present invention. Gelatin that can be used in the present invention may be alkali or acid processed. If ossein gelatin is to be used, it is preferably freed of calcium or iron. The preferred calcium content is 1 - 999 ppm, with the range of 1 - 500 ppm

being particularly preferred. The preferred iron content is 0.01 - 50 ppm, with the range of 0.1 - 10 ppm being particularly preferred. The calcium or iron content can be adjusted by passing an aqueous gelatin solution of interest through an ion-exchanger.

The following developing agents may be used to develop the light-sensitive material of the present invention: catechol, derivatives thereof (e.g. 4-chlorocatechol, 4-phenyl-catechol and 3-methoxycatechol), pyrogallol, derivatives thereof (e.g. 4-acetylpyrogallol), ascorbic acid, derivatives thereof (e.g. sodium ascorbate), chlorohydroquinone, bromohydroquinone, methylhydroquinone, 2,3-dibromohydroquinone and 2,5-diethylhydroquinone;

$\text{HO}-(\text{CH}=\text{CH})_n-\text{NH}_2$ type developing agents, representative examples of which are ortho- and para-aminophenols such as 4-aminophenol, 2-amino-6-phenylphenol, 2-amino-4-chloro-6-phenylphenol and N-methyl-p-aminophenol;

$\text{H}_2\text{N}-(\text{CH}=\text{CH})_n-\text{NH}_2$ type developing agents, such as 4-amino-2-methyl-N,N-diethylaniline, 2,4-diamino-N,N-diethylaniline, N-(4-amino-3-methylphenyl)-morpholine, and p-phenylenediamine; and heterocyclic developing agents such as 3-pyrazolidones (e.g. 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.

Other developing agents that can be used effectively in the present invention are described in T.H. James, "The Theory of the Photographic Process", Fourth Edition, pp. 291-334, Macmillan Publishing Co., Inc., 1977, and Journal of the American Chemical Society, Vol. 73, p. 3,100,1951.

The developing agents described above may be used either on their own or as admixtures. Preferably, they are used as admixtures.

The developing solutions to be used in developing the light-sensitive material of the present invention may contain sulfites as preservatives without compromising the advantages of the present invention. Hydroxylamine or hydrazide compounds may also be used as preservatives. Preservatives are preferably used in amounts of 5 - 500 g, more preferably 20 - 200 g, per liter of the developing solution.

The developing solutions may also contain glycols as organic solvents and suitable glycols include ethylene glycol, diethylene glycol, propylene glycol, triethylene glycol, 1,4-butanediol and 1,5-pentanediol, with diethylene glycol being preferably used. These glycols are preferably used in amounts of 5 - 500 g, more preferably 20 - 200 g, per liter of the developing solution. These glycols may be used either on their own or as admixtures.

The light-sensitive material of the present invention can be provided with very high storage stability by processing it with developing solutions that contain the development restrainers described above. The developing solutions formulated as described above preferably have pH values of 9 - 13, with the range of 10 - 12 being more preferred from the viewpoints of preserving effect and other photographic characteristics. As for cations in the developing solution, potassium ions are more effective in enhancing the activity of developing solutions than sodium ions and hence the content of potassium ions is preferably as high as possible.

The light-sensitive material of the present invention can be processed under various conditions. As for the temperature for processing, say development, it is preferably 50°C or below, with the range of ca. 25 - 40°C being particularly preferred. The development will in most cases end within 2 minutes but satisfactory results can often be obtained by rapid processing that lasts for 10-50 seconds. Other processing steps than development, such as washing with water, stopping, stabilization and fixing may be performed under appropriate conditions. If necessary, prehardening, neutralization and other additional steps may be employed. Some of these steps other than development may be omitted as required. Development may be manual (as in tray development or rack development) or mechanical (as in roller development or hanger development).

The concept of the present invention is applicable to all kinds of light-sensitive materials that have at least one light-sensitive silver halide emulsion layer provided on a support, as exemplified by color photographic materials, X-ray photographic materials, and photographic materials for use in photomechanical processes to make printing plates.

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

Example 1

Samples of negative-acting silver halide photographic material for use as light-sensitive materials to be subjected to contact exposure in a daylight room were prepared by the following procedure.

Preparation of emulsion

A silver chlorobromide emulsion containing 2 mol% AgBr was prepared as follows.

5 An aqueous solution containing 23.9 mg of potassium pentabromorhodate per 60g of silver nitrate, sodium chloride and potassium bromide and an aqueous solution of silver nitrate were mixed in an aqueous gelatin solution under agitation by a double-jet method at 40°C for 25 minutes to prepare a silver chlorobromide emulsion comprising grains with an average size of 0.20 μm .

10 To the emulsion, 200 mg of 6-methyl-4-hydroxy-1,3,3a,7-tetraazaindene (stabilizer) was added and the mixture was washed with water and desalted. To the desalted mixture, 20 mg of 6-methyl-4-hydroxy-1,3,3a,7-tetraazaindene was added and the mixture was subjected to sulfur sensitization. Thereafter, the necessary amount of gelatin was added and 6-methyl-4-hydroxy-1,3,3a,7-tetraazaindene was further added as a stabilizer. Subsequently, the mixture was worked up with water to a total volume of 260 ml, whereby a complete emulsion was obtained.

15 Preparation of latex (L) for addition to the emulsion

A sodium salt of dextran sulfate (0.25 kg; KMDS of Meito Sangyo Co., Ltd.) and 0.05 kg of ammonium persulfate were added to 40 L of water. To the stirred solution (81°C), a mixture of 4.51 kg of n-butyl acrylate, 5.49 kg of styrene and 0.1 kg of acrylic acid was added under a nitrogen stream over a period of 1 h. Thereafter, 20 0.005 kg of ammonium persulfate was added and the mixture was stirred for 1.5 h, cooled and adjusted to a pH of 6 with aqueous ammonia.

The resulting latex solution was filtered through Whatman GF/D filter and worked up with water to a total volume of 50.5 kg, whereby a monodispersed latex (L) comprising particles with an average size of 0.25 μm was prepared.

25 The additives listed below were added to the previously prepared emulsion and a coating solution for silver halide emulsion layer was prepared as described below.

Preparation of emulsion coating solution

30 Nine milligrams of compound (A) was added as a biocide to the previously prepared emulsion. The pH of the mixture was adjusted to 6.5 with 0.5 N sodium hydroxide. Subsequently, 360 mg of compound (T-2) was added. Further, 5 ml of a 20% solution of saponin, 180 mg of sodium dodecylbenzenesulfonate, 80 mg of 5-methylbenzotriazole and 43 ml of latex solution (L) were added, with all amounts being based on one mole of silver halide. Thereafter, 60 mg of compound (M) and 280 mg of a water-soluble styrene-maleic acid copolymer (thickener) were successively added and the mixture was worked up with water to a total volume of 475 ml to prepare coating solution for emulsion layer.

Then, a coating solution for emulsion protective layer was prepared in the following manner.

Preparation of emulsion protective coating solution

40 Pure water (280 ml) was added to gelatin (50 g) to swell it and the swollen gelatin was dissolved at 40°C. Thereafter, a 1% aqueous solution of compound (Z) (coating aid), compound (N) (filter dye) and compound (D) were successively added, and the pH of the resulting solution was adjusted to 6.0 with aqueous citric acid. Further, the two matting agents identified in Table 1 which comprised of irregular shaped particles were added, 45 either individually or in combination, to give the coat weights also shown in Table 1, whereby six samples P-1 to P-6, of a coating solution for emulsion protective layer were prepared.

50

55

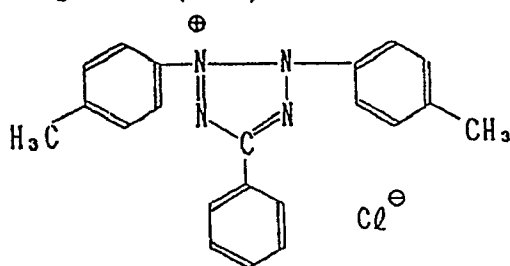
Table 1

Coating solution	Coat weight of matting agent, mg/m ²	
	S-1	S-2
P-1	10	0
P-2	20	0
P-3	10	2
P-4	0	4
P-5	0	10
P-6	0	20

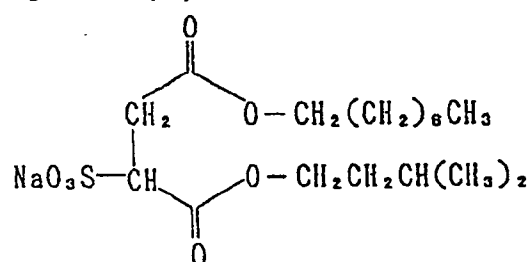
S-1: Matting agent having an average particle size of
3 μm ($\cong$ 4 μm particles were removed by sieving)

S-2: Matting agent having an average particle size of
6 μm ($\cong$ 4 μm particles were removed by sieving)

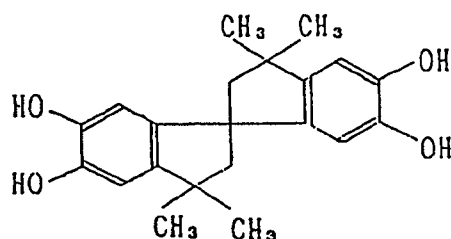
Compound (T-2)



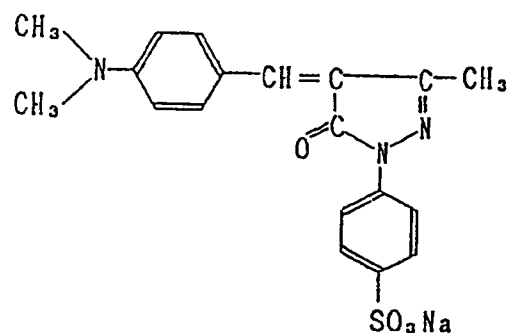
Compound (Z)



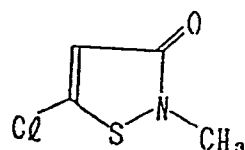
Compound (M)



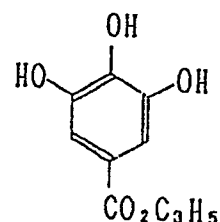
Compound (N)



Compound (A)



Compound (D)

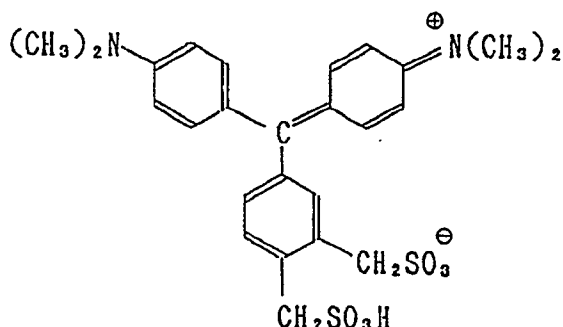


A coating solution for backing layer was subsequently prepared in the following manner.

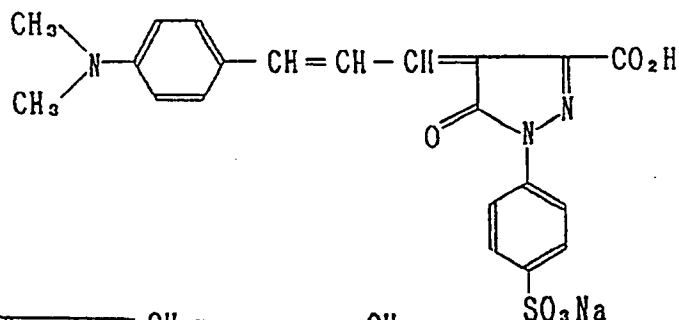
Preparation of backing coating solution B-1

Gelatin (36 g) was swollen in water and heated to dissolve in water. Thereafter, three dye compounds (C-1), (C-2) and (C-3) were added to water in respective amounts of 1.6 g, 310 mg and 1.9 g, and 2.9 g of compound (N) was also added as an aqueous solution. The resulting aqueous solution was added to the gelatin solution. Subsequently, 11 ml of a 20% aqueous solution of saponin, 5 g of compound (C-4) as a physical property modifier and 63 mg of a methanol solution of compound (C-5) were added. To the resulting solution, 800 g of a water-soluble styrene-maleic acid copolymer was added as a thickener to adjust the viscosity of the solution. Further, the pH of the solution was adjusted to 5.4 with an aqueous solution of citric acid. Finally, 144 mg of glyoxal and an epoxy compound (E-5) were added and the solution was worked up with water to a total volume of 960 ml to prepare a backing (BC) coating solution B-1.

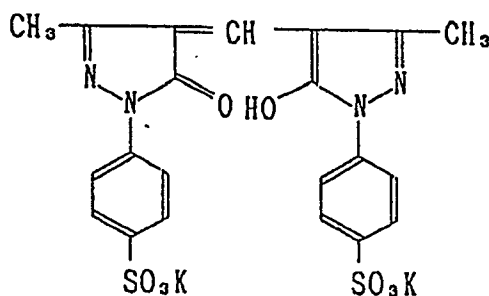
Compound (C-1):



Compound (C-2):



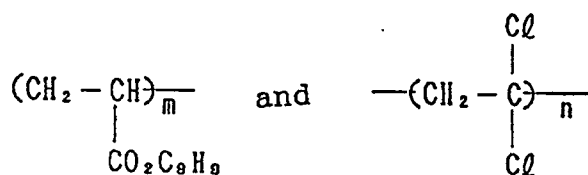
Compound (C-3):



Compound (C-4):

Copolymer latex of

5

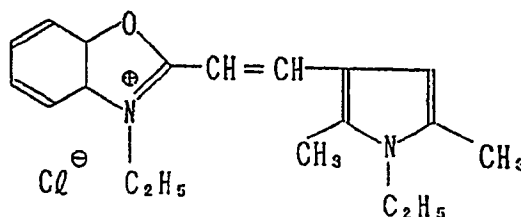


10

Compound (C-5):

(m : n = 1 : 1)

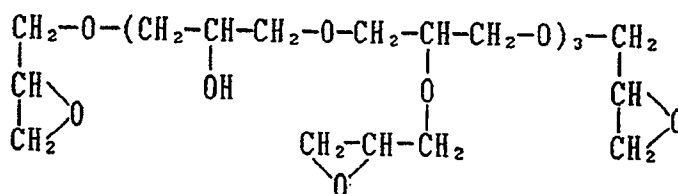
15



20

Compound (E-5):

25



30

Subsequently, a coating solution B-2 for backing protective layer was prepared in the following manner

Preparation of coating solution B-2

35

Gelatin (50 g) was swollen in water and heated to dissolve in water. Thereafter, a sodium salt of bis(2-ethylhexyl)-2-sulfosuccinate, sodium chloride, glyoxal and mucochloric acid were added in respective amounts of 340 mg, 3.4 g, 1.1 g and 540 mg. To the resulting mixture, a polymethyl methacrylate powder comprising spherical particles with an average size of 4 μm was added as a matting agent to provide a coat weight of 40 mg/m². The mixture was worked up with water to a total volume of 1,000 ml to prepare coating solution B-2 for backing protective layer.

40

Preparation of support having an antistatic layer

45

Subbed polyethylene terephthalate films were subjected to corona discharge with an energy of 50 W/m² per minute. Thereafter, antistatic solutions having the composition shown below were coated onto the base films at a rate of 30 m/min using a roll fitted coating pan and air knife to give the coat weights also shown below.

50

Water-soluble conductive polymer (A) 0.6 g/m²

Hydrophobic polymer particles (B) 0.3 g/m²

Hardening agent (H) 0.15 g/m²

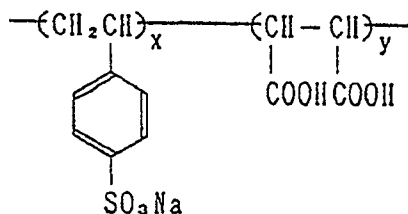
55

Nonionic surfactant (C) 0.06 g/m²

The applied coatings were dried at 90°C for 2 minutes and heated at 140°C for 90 seconds to prepare supports having antistatic layers.
Water-soluble conductive

5

10



$$x:y=67:33$$

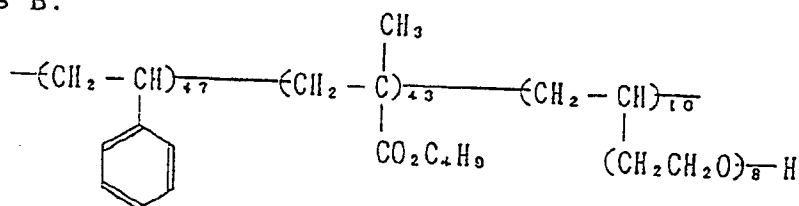
$$\bar{M}_n=5 \times 10^3$$

Hydrophobic

15

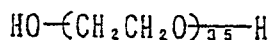
polymer particles B:

20



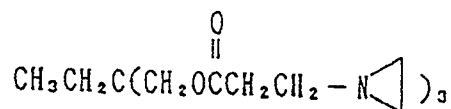
Nonionic surfactant C:

25



Hardener H:

30



35

Preparation of test samples

40

Backing (BC) layer coating solution B-1 and backing (BC) protective layer coating solution B-2 were applied simultaneously onto one side of each of the supports which had the antistatic layers described above. The emulsion coating solution and the emulsion protective layer coating solution were applied simultaneously in superposition on the other side of each support.

45

Coating and drying conditions

50

After applying a coating solution at 35°C, cold air (5°C) was blown for 6 sec to cool and solidify the applied solution; thereafter, using drying air having a dry-bulb temperature of 23°C and a relative humidity of 20%, the applied coat was dried at a surface temperature of 10°C until the weight ratio of water to gelatin in the coat decreased to 1,600%; subsequently, using drying air having a temperature of 27°C and a relative humidity of 20%, the coat was dried until the water to gelatin weight ratio dropped to 800%; then, drying was performed under conditions A (see below) at 34°C; 5 seconds after the average surface temperature of the coated layer being dried rose to 33°C, the drying condition were shifted to B.

55

Table 2. Drying Conditions A*

Run	Temperature of the coated surface, °C	Drying time, sec
A-1	25	30
A-2	25	50
A-3	19	30
A-4	19	45
A-5	19	90
A-6	10	50

* The drying time over which the weight ratio of water to gelatin in the coated layer was reduced from 800% to 200% and the temperature of the coated surface during this period.

Table 3. Drying Conditions B

Run	Dry-bulb temperature(°C)	Relative humidity, %	Drying time, sec	DP, °C	Remarks
B-1	35	22	20	15	Invention
B-2	35	22	60	15	do.
B-3	35	22	2	15	Comparison
B-4	35	22	20	16	Invention
B-5	80	22	20	16	do.
B-6	35	40	20	16	do.
B-7	35	22	20	18	Comparison
B-8	80	22	20	18	do.

Methods of evaluation

The test samples thus prepared were developed and subjected to other steps of photographic processing. Thereafter, they were subjected to a storage stability test under accelerated conditions, a peel electrical charging test, and a dust adhesion test which was conducted to evaluate the overall charging characteristics of the samples. The results are shown in Table 4.

Photographic processing

Development and fixing were conducted using the processing solutions formulated as follows.

Formula of developing solutionRecipe A

15	Pure water (ion-exchanged water)	150 ml
	Ethylenediaminetetraacetic acid disodium salt	2 g
20	Diethylene glycol	50 g
	Potassium sulfite (55% w/v aq. sol.)	100 ml
25	Potassium carbonate	50 g
	Hydroquinone	15 g
	5-Methylbenzotriazole	200 mg
30	1-Phenyl-5-mercaptotetrazole	30 mg
	Potassium hydroxide	q.s. to adjust the
35		pH of developing
		solution to 10.9
	Potassium bromide	4.5 g

40

Recipe B

45	Pure water (ion-exchanged water)	3 ml
	Diethylene glycol	50 g
	Ethylenediaminetetraacetic acid disodium salt	25 mg
50	Acetic acid (90% aq. sol.)	0.3 ml
	5-Nitroindazole	110 mg
55	1-Phenyl-3-pyrazolidone	500 mg

Just before use, recipes A and B were successively dissolved in 500 ml of water and the mixture was worked up to a total volume of 1,000 ml.

Formula of fixing solutionRecipe A

5	Ammonium thiosulfate (72.5% w/v aq. sol.)	230 ml
	Sodium sulfite	9.5 g
10	Sodium acetate (3H ₂ O)	15.9 g
	Boric acid	6.7 g
15	Sodium citrate (2H ₂ O)	2 g
	Acetic acid (90% w/w aq. sol.)	8.1 ml

Recipe B

20	Pure water (ion-exchanged water)	17 ml
	Sulfuric acid (50% w/w aq. sol.)	5.8 g
25	Aluminum sulfate (aq. sol. with 8.1% w/w of Al ₂ O ₃)	26.5 g

30 Just prior to use, recipes A and B were successively dissolved in 500 ml of water and the mixture was worked up to a total volume of 1,000 ml. The worked up fixing solution had a pH of ca. 4.3

Processing scheme

35	<u>Step</u>	<u>Temperature, °C</u>	<u>Time, sec</u>	<u>Tank capacity, L</u>
	Development	34	15	20
40	Fixing	34	15	20
	Washing	R.T.	10	15
	Drying	40	10	

45 The time of each step included the "solution crossover time" to the subsequent step.

Storage stability test under accelerated conditions

50 The packaged samples were divided into two groups, one of which was stored frozen at -26°C and the other group was stored in a thermostated bath at 40°C for 3 days. The samples of each group were photographically processed and rehumidified at 23°C and 55% r.h. for 1 day. In the same environment, the specific surface resistance of each sample was measured with a teraohmmeter Model VE-30 of Kawaguchi Electric Works Co., Ltd.

55 Peel electric charging test

The processed samples were rehumidified at 23°C and 20% r.h. for 1 day and subjected to 10 cycles of

contact and peeling from neoprene rubber in the same environment. The amount of electric charges collected on the surface of each sample was then measured.

Dust adhesion test

Films that had been heated under accelerated conditions were processed photographically and rehumidified at 23°C and 20% r.h. for 1 day. The emulsion coated side of each film was rubbed with a cotton cloth 20 times and immediately put above absorbent wadding (0.5 g). When the wadding was attracted by film, the distance between the two members are measured.

Table 4

No.	Matting agent	Drying condition A	Drying condition B	Peel charging property, coulomb/m ²	Specific surface resistance, Ω		Dust adhesion, cm	Remarks
					Before heat treatment	After heat treatment		
1	P-1	A-4	B-4	270	4×10^{11}	5×10^{11}	15	Comparison
2	P-2	A-4	B-4	270	4×10^{11}	5×10^{11}	15	do.
3	P-5	A-1	B-4	270	4×10^{11}	5×10^{11}	15	do.
4	P-5	A-2	B-4	270	4×10^{11}	5×10^{11}	15	do.
5	P-5	A-3	B-4	265	4×10^{11}	5×10^{11}	15	do.
6	P-5	A-4	B-4	165	4×10^{11}	5×10^{11}	0.8	Invention
7	P-5	A-5	B-4	160	4×10^{11}	5×10^{11}	0.5	do.
8	P-5	A-6	B-4	165	4×10^{11}	5×10^{11}	0.8	do.
9	P-3	A-2	B-4	270	4×10^{11}	5×10^{11}	15	Comparison
10	P-3	A-6	B-4	265	4×10^{11}	5×10^{11}	15	Comparison
11	P-4	A-2	B-4	270	4×10^{11}	5×10^{11}	15	Comparison
12	P-4	A-6	B-4	170	4×10^{11}	5×10^{11}	1.0	Invention

5

Table 4

No.	Matting agent	Drying condition A	Drying condition B	Peel charging property, coulomb/m ²	Specific surface resistance, Ω		Dust adhesion, cm	Remarks
					Before heat treatment	After heat treatment		
13	P-6	A-2	B-4	265	4×10^{11}	5×10^{11}	15	Comparison
14	P-6	A-6	B-4	160	4×10^{11}	5×10^{11}	0.5	Invention
15	P-5	A-6	B-1	165	4×10^{11}	5×10^{11}	0.8	do.
16	P-5	A-6	B-2	165	4×10^{11}	5×10^{11}	0.8	do.
17	P-5	A-6	B-3	165	4×10^{11}	2×10^{12}	20	Comparison
18	P-5	A-6	B-4	165	4×10^{11}	5×10^{11}	0.8	Invention
19	P-5	A-6	B-5	165	4×10^{11}	5×10^{11}	0.8	do.
20	P-5	A-6	B-6	165	4×10^{11}	5×10^{11}	0.8	Invention
21	P-5	A-6	B-7	165	4×10^{11}	1.5×10^{12}	17	Comparison
22	P-5	A-6	B-8	165	4×10^{11}	1.5×10^{12}	17	do.

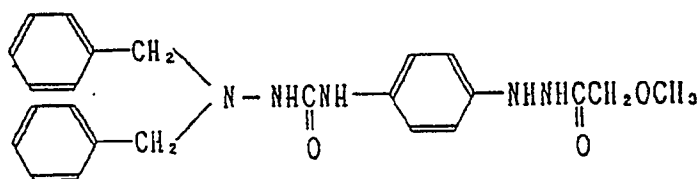
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Example 2

Additional samples were prepared as in Example 1 except that hydrazine compound (H-47) was used as a contrast-increasing agent in place of tetrazolium compound (T-2). The results were similar to those obtained in Example 1. The development step was conducted at 38°C for 20 seconds using developing solution B having the recipe shown below.

Compound (H-47):

50



Developing solution B

5	Hydroquinone	45.0 g
	N-Methyl-p-aminophenol hemisulfate	0.8 g
	Sodium hydroxide	15.0 g
10	Potassium hydroxide	55.0 g
	5-Sulfosalicylic acid	45.0 g
	Boric acid	35.0 g
15	Potassium sulfite	110.0 g
	Ethylenediaminetetraacetic acid disodium salt	1.0 g
20	Potassium bromide	6.0 g
	5-Methylbenzotriazole	0.6 g
	n-Butyl diethanolamine	15.0 g
25	Water	to make 1,000 ml (pH = 11.6)

Example 3

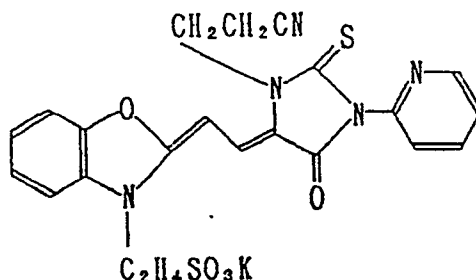
30 Samples of negative-acting film for darkroom photography were prepared as in Example 1 except in the following points: the amount of potassium pentabromorhodate used in the making of an emulsion was 25 µg per 60 g of silver nitrate; silver chlorobromide containing 25 mol% AgBr was used; spectral sensitizer (C) was added during chemical sensitization. The results of experiments conducted on the samples were entirely the same as in Example 1.

35

Spectral sensitizer (C):

40

45

Example 4

50

Samples of high-sensitivity negative-acting film for use in daylight room were prepared by the following procedure.

Preparation of samples

55

Solution B (see below) was added to solution A (also see below) in an atmosphere rendered acidic with nitric acid (pH 3.0) while the silver potential (EAg) was held at 170 mV. Mixing was performed by a double-jet method with EAg being controlled using 1 N NaCl. Solution C (see below) was also added at the same reaction

temperature and flow rate for the first 2 minutes of addition; thereafter, solution C was added at a rate 0.99 times as fast as the initial rate, with the EAg of solution B being controlled with 1 N NaCl. The silver halide emulsions thus prepared comprised silver halide grains having an average size of 0.08 μm .

5 Solution A

	Gelatin	5.6 g
10	Polyisopropylene/polyethyleneoxy-	
	disuccinic acid ester (Na salt) in	
	10% ethanol solution	0.56 ml
15	Sodium chloride	0.12 g
	Conc. nitric acid	0.43 ml
20	Distilled water	445 ml

Solution B

	Silver nitrate	60 g
25	Conc. nitric acid	0.208 ml
	Distilled water	85.2 ml

Solution C

30	Gelatin	3 g
	Polyisopropylene/polyethyleneoxy-	
35	disuccinic acid ester (Na salt) in	
	10% ethanol solution	0.3 ml
	Potassium bromide	4.2 g
40	Sodium chloride	18.6 g
	Na_3RhCl_6 (1% aq. sol.)	0.02 ml
45	Distilled water	87.3 ml

50

55

Solution D

5	Gelatin	1.4 g
	Polyisopropylene/polyethyleneoxy-	
	disuccinic acid ester (Na salt) in	
10	10% ethanol solution	0.14 ml
	Distilled water	48.8 ml

15 The silver halide grains thus formed contained 90 mol% AgCl and 2×10^{-6} moles of rhodium per mole of silver halide. Their monodispersity was 8 - 15%.

For EAg measurements, a metallic silver electrode and a double-junction type saturated Ag/AgCl reference electrode were used (the electrode configuration was the double-junction type described in JP-A-57-197543).

Solutions B and C were added using a variable-flow, roller tube type metering pump.

20 During the addition of solutions B and C, portions of each emulsion were sampled and examined under an electron microscope. Since no new grains had formed, it was verified that the addition of those solutions did not exceed the critical growth rate of grains in the system.

To each of the thus prepared emulsions, a - c, 6-methyl-4-hydroxy-1,3,3a,7-tetraazaindene was added in an amount of 200 mg per mole of silver halide. After pH adjustment to 5.7 with sodium carbonate, solution D was added. Then, each silver halide emulsion was washed with water and desalted in the usual manner. Sub-
 25 sequently, 6-methyl-4-hydroxy-1,3,3a,7-tetraazaindene and potassium bromide were added in respective amounts of 58 mg and 150 mg per mole of silver halide, and sulfur sensitization was then performed. Thereafter, 6-methyl-4-hydroxy-1,3,3a,7-tetraazaindene (stabilizer) and gelatin were added in respective amounts of 570 mg and 25 g per mole of silver halide. Further, the additives identified below were added to prepare coating solutions for emulsion layer. In addition, respective coating solutions for an emulsion protective layer, a backing
 30 layer and a backing protective layer were prepared in entirely the same manner as in Example 1. Supports which were also the same as those used prepare samples as Example 1. When the samples were processed and tested as in Example 1, the results were entirely the same as obtained in Example 1.

35

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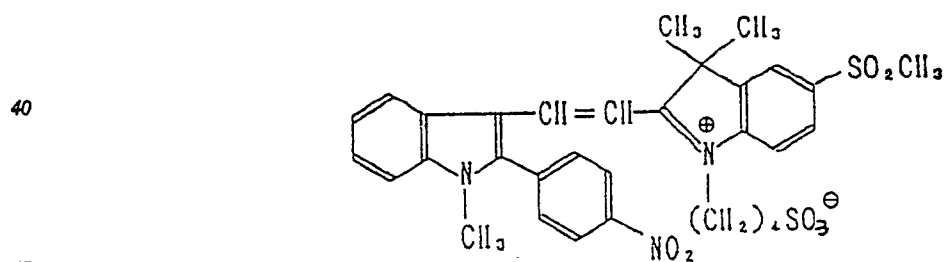
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Additives to emulsion coating solution

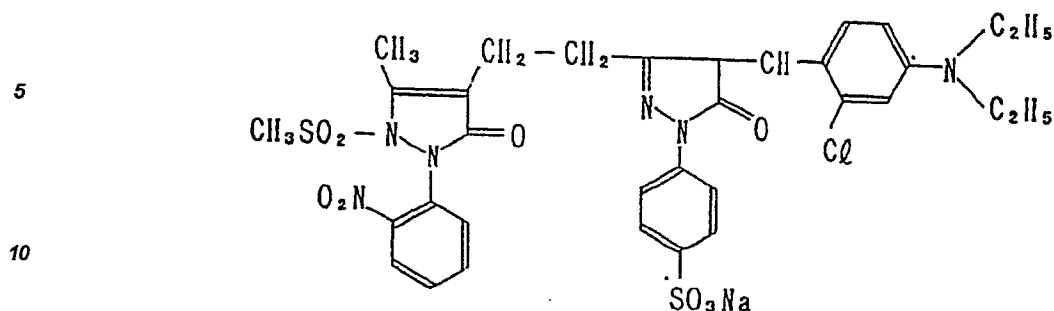
5	Saponin	100 mg/m ²
	Potassium bromide	3 mg/m ²
10	Desensitizing dye (DS-1)	1 mg/m ²
	Sodium hydroxide	10 mg/m ²
	Tetrazolium compound (T-2)	45 mg/m ²
15	Sodium dodecylbenzenesulfonate	21 mg/m ²
	Butyl acrylate/styrene/acrylic	-
20	acid copolymer latex	1 g/m ²
	5-Methylbenzotriazole	10 mg/m ²
25	5-Phenyl-1-mercaptotetrazole	11.5 mg/m ²
	2-Mercaptobenzimidazole-5-sulfonic acid	1 mg/m ²
30	Benzyl-triphenylphosphonium chloride	5 mg/m ²
	Compound (M) (see above)	5.8 mg/m ²

35 DS-1Example 5

50 Additional samples were prepared as in Example 4 except in the following points: the desensitizing dye (DS-1) and the tetrazolium compound (T-2) in the emulsion coating solutions were replaced by 10 mg/m² of hydrazine compound (H-47) ; and compound (O) identified below was added in an amount of 20 mg/m² to the emulsion protective layer coating solution.

55

Compound (O):



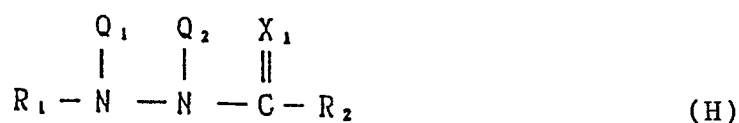
Evaluation

15 The samples were evaluated by the same method as in Example 4 except that development was performed at 38°C for 20 seconds using developing solution B (as used in Example 2). The results were the same as in Example 4.

20 As is clear from the foregoing description, the present invention provides a packaged light-sensitive material that is ideally protected against static buildup in that the film itself is not easily charged electrically and that it will experience less deterioration in specific surface area with time. The invention also provides a process for producing such an improved packaged light-sensitive material.

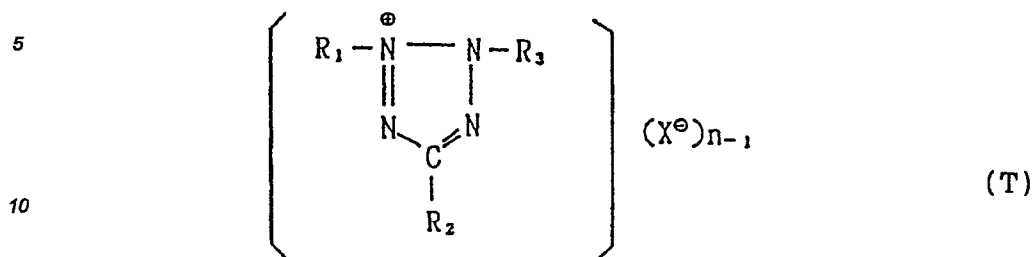
Claims

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1. A process for manufacturing a packaged silver halide photographic material comprising a step of producing a silver halide photographic material having a support, hydrophilic colloidal layers at least one of which is a light-sensitive silver halide emulsion layer, and an antistatic layer thereon, and a step of packaging said silver halide photographic material, wherein said producing step comprises:
 - 1) providing a hydrophilic colloidal layer on said support; drying said hydrophilic colloidal layer by contacting said hydrophilic colloidal layer with air heated at 35-80°C and/or has a relative humidity of 5-25% for not less than 5 seconds within 5 minutes after the average surface temperature of said hydrophilic colloidal layer becomes lower than a temperature for said drying by 1°C;
 - 2) providing the outermost layer on the side of said support, which has the light-sensitive silver halide emulsion layer, containing 4-80 mg/m² of matting agent having a particle size of not smaller than 4 μm; drying said outermost layer by keeping a temperature of not higher than 19°C to decrease the water to gelatin weight ratio from 800% to 200% and the drying time of not shorter than 35 seconds; and
 - 3) said packaging step comprises maintaining said silver halide photographic material in an atmosphere having a dew point not higher than 16°C until the end of packaging said silver halide photographic material.
 2. A process according to claim 1 wherein said antistatic layer contains at least a water-soluble conductive polymer, a hydrophobic polymer latex and a curing agent.
 3. A process according to claim 2 wherein said curing agent is a polyfunctional aziridine compound.
 4. A process according to claim 1 wherein at least one of said light-sensitive silver halide emulsion layers contains a hydrazine compound represented by the following general formula (H):



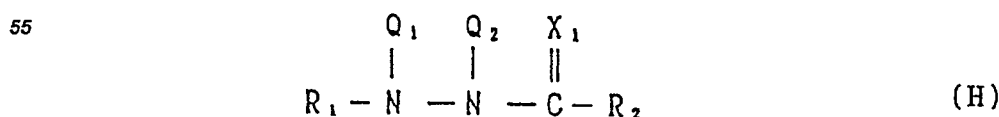
55 where R₁ is a monovalent organic residue; R₂ is a hydrogen atom or a monovalent organic residue; Q₁ and Q₂ are each a hydrogen atom, an optionally substituted alkylsulfonyl group, or an optionally substituted arylsulfonyl group; X₁ is an oxygen atom or a sulfur atom.

5. A process according to claim 1 wherein at least one of said light-sensitive silver halide emulsion layers contains a tetrazolium compound represented by the following general formula (T):



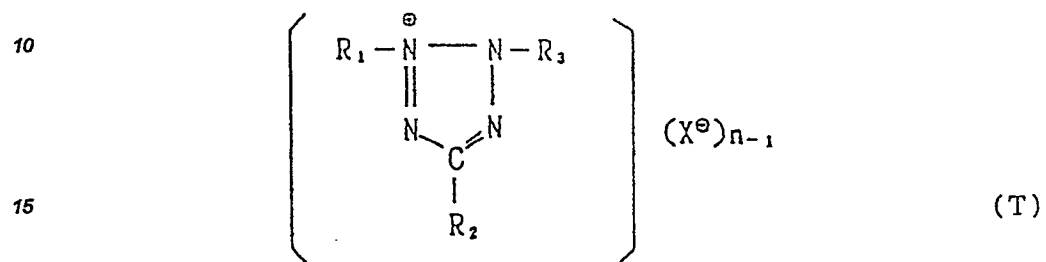
where R_1 , R_2 and R_3 are each a substituted or unsubstituted phenyl group; and $X^\ominus$ is an anion.

6. A packaged silver halide photographic material comprising a silver halide photographic material having a support, hydrophilic colloidal layers at least one of which is a light-sensitive silver halide emulsion layer, and an antistatic layer thereon, wherein said silver halide photographic material is produced by a step comprising:
- 1) providing a hydrophilic colloidal layer on said support; drying said hydrophilic colloidal layer by contacting said hydrophilic colloidal layer with air heated at 35-80°C and/or has a relative humidity of 5-25% for not less than 5 seconds within 5 minutes after the average surface temperature of said hydrophilic colloidal layer becomes lower than a temperature for said drying by 1°C;
 - 2) providing the outermost layer on the side of said support, which has the light-sensitive silver halide emulsion layer, containing 4-80 mg/m² of matting agent having a particle size of not smaller than 4 µm; drying said outermost layer by keeping a temperature of not higher than 19°C to decrease the water to gelatin weight ratio from 800% to 200% and the drying time of not shorter than 35 seconds; and
 - 3) said packaging step comprises maintaining said silver halide photographic material in an atmosphere having a dew point not higher than 16°C until the end of packaging said silver halide photographic material.
7. A packaged silver halide photographic material according to claim 6 wherein said antistatic layer contains at least a water-soluble conductive polymer, a hydrophobic polymer latex and a curing agent.
8. A packaged silver halide photographic material according to claim 7 wherein said water-soluble conductive polymer has a molecular weight of 3,000 - 100,000.
9. A packaged silver halide photographic material according to claim 7 wherein said water-soluble conductive polymer is contained in an amount of 0.01 - 10 g/m².
10. A packaged silver halide photographic material according to claim 7 wherein said hydrophobic polymer latex has a molecular weight of at least 3,000.
11. A packaged silver halide photographic material according to claim 7 wherein said hydrophobic polymer latex is contained in an amount of 0.01 - 10 g/m².
12. A packaged silver halide photographic material according to claim 7 wherein said curing agent is a polyfunctional aziridine compound.
13. A packaged silver halide photographic material according to claim 6 wherein at least one of said light-sensitive silver halide emulsion layers contains a hydrazine compound represented by the following general formula (H):



where R_1 is a monovalent organic residue; R_2 is a hydrogen atom or a monovalent organic residue; Q_1 and Q_2 are each a hydrogen atom, an optionally substituted alkylsulfonyl group, or an optionally substituted arylsulfonyl group; X_1 is an oxygen atom or a sulfur atom.

- 5 **14.** A packaged silver halide photographic material according to claim 6 wherein at least one of said light-sensitive silver halide emulsion layers contains a tetrazolium compound represented by the following general formula (T):



where R_1 , R_2 and R_3 are each a substituted or unsubstituted phenyl group; and $X^{\ominus}$ is an anion.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91 30 3139

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	EP-A-317247 (KONICA CORPORATION) * page 14, lines 20 - 26; claims 1-14 * ----	1-14	G03C1/74 G03C1/95
X,Y	PATENT ABSTRACTS OF JAPAN vol. 14, no. 226 (P-1047)(4169) 14 May 1990, & JP-A-02 054249 (FUJI PHOTO FILM COMPANY LTD.) 23 February 1990, * the whole document * ----	1-14	
Y	US-A-4225665 (F.L.SCHADT,III) * the whole document * -----	1-14	
D	& JP-A-550846588 -----		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C
Place of search	Date of completion of the search	Examiner	
THE HAGUE	18 JULY 1991	BUSCHA A.J.	
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 I : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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