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(54) Silver halide photographic photosensitive material.

(57) A silver halide photographic photosensitive material is disclosed, comprising a support having thereon at least one hydrophilic colloid layer, at least one layer of which is a photosensitive silver halide emulsion layer comprising tabular silver halide grains having an aspect ratio of at least 3, said photosensitive silver halide emulsion layer being prepared by reacting a water soluble silver salt with a water soluble alkali halide to form an emulsion comprising tabular silver halide grains, de-salting the thus formed emulsion, chemically sensitizing the emulsion and coating the resulting chemically sensitized emulsion comprising tabular silver halide grains onto the support, wherein a chloride of an element or ion selected from the group consisting of Na, K, Mg, Ca, Li and NH_4^+ is added to said emulsion either immediately after de-salting, after de-salting but prior to chemical sensitization, during chemical sensitization, after chemical sensitization but prior to coating, or immediately prior to coating.

SILVER HALIDE PHOTOGRAPHIC PHOTOSENSITIVE MATERIAL

FIELD OF THE INVENTION

The present invention concerns a silver halide photographic photosensitive material employing tabular silver halide grains, which photographic material provides improved pressure resistance characteristics.

BACKGROUND OF THE INVENTION

Generally, a photographic photosensitive material coated with a silver halide emulsion is subjected to various handling, which handling applies pressure to the emulsion. For example, general purpose negative films can be wound into a cartridge, or are occasionally folded when placed into the camera. Additionally, general purpose negative films can be stretched by frame feeding and can contact transporting parts within the camera.

On the other hand, sheet films, such as sensitive materials for printing purposes and X-ray sensitive materials for direct medical use, are handled directly by hand, such that these materials are occasionally subjected to folding. Furthermore, sheet films are forcibly contacted with metal and rubber, for example, in light room transporting devices and high speed changers.

Additionally, photosensitive materials are subjected to considerable pressure in the cutting and finishing operations.

When a photographic photosensitive material is subjected to such applied pressures, the pressure is applied upon the silver halide grains via the gelatin or polymeric material which forms the binder medium for the silver halide grains. It is known that a blackening phenomena which does not correspond to the amount of exposure and a loss of photographic speed occur when a pressure is applied to the silver halide grains as reported, for example, by K.B. Mather, J. Opt. Soc. Am., 38, 1054 (1948), P. Faelens and P. de Smet in Sci. et Ind. Phot., 25, No. 5, 178 (1954) and P. Faelens in J. Phot. Sci., 2, 105 (1954).

Consequently, it is desirable to provide a photographic photosensitive material having a high pressure resistance.

On the other hand, there is a demand for increasingly higher speed emulsions. By increasing photographic speed, it is possible to take photographs even at night without using flash, and to take photographs of fast moving objects using a high shutter speed. With X-ray films, it is possible to reduce the X-ray dose rate such that the effect of X-rays on the human body is minimized.

However, in general, there is an undesirable correlation between photographic speed and pressure sensitivity in that pressure sensitivity increases as the photographic speed of an emulsion is increased.

Moreover, fogging of the silver halide grains due to the use of sensitizing dyes becomes pronounced upon application of pressure. Large amounts of a sensitizing dye are added to provide color sensitization. When the amount of absorbed light is increased and the photographic speed is raised by adding a large amount of sensitizing due, there is an inevitable increase in blackening development upon the application of pressure. Methods in which the applied pressure is prevented from reaching the grains, such as methods in which plasticizers such as polymers or emulsified materials are introduced, and methods in which the silver halide grain silver halide/gelatin ratio is reduced, are known as means of improving the pressure characteristics.

A method employing heterocyclic compounds to reduce pressure sensitivity is disclosed in British Patent 738,618, a method employing alkyl phthalates is disclosed in British Patent 738,637, a method employing alkyl esters is disclosed in British Patent 738,639, a method employing polyhydric alcohols is disclosed in U.S. Patent 2,960,404, a method employing carboxyalkylcellulose is disclosed in U.S. Patent 3,121,060, a method employing paraffins and carboxylic acid salts is disclosed in JP-A-49-5017 and a method employing alkyl acrylates and organic acids is disclosed in JP-B-53-28086. (The term "JP-A" and "JP-B" as used herein signify an "unexamined published Japanese patent application" and an "examined Japanese patent publication", respectively.)

However, the methods in which plasticizers are added reduce the mechanical strength of the emulsion layer, such that the amount of plasticizer which can be used is limited. Furthermore, the rate of development and the photographic speed are disadvantageously reduced when the amount of gelatin is increased, such that neither of these methods is satisfactory.

Generally, cubic, octahedral and spherical silver halide grains such as potato shaped grains are more resistant to deformation from their original shape due to the application of an external force than tabular grains which have a large projected area diameter/thickness ratio, and these grains are also less sensitive to applied pressure. Consequently, by employing a plasticizer or by increasing the gelatin content as described above, it is possible to improve the pressure characteristics of pressure resistant cubic, octahedral and spherical pressure resistant grain to a level which is fairly satisfactory although still inadequate.

Tabular grains provide a larger covered area per unit volume of silver halide such that a high optical sensitivity can be obtained with a smaller silver content as disclosed, for example, in U.S. Patents 4,434,226, 4,439,520 and 4,425,425.

Furthermore, by having a large surface area per unit volume it is possible to adsorb more sensitizing dye during spectral sensitization to thereby increase the capturing capacity for incident light. In order to activate these characteristics, the sensitizing dye is preferably added in an amount of at least 60%, preferably at least 80% and most desirably at least 100%, of the saturated adsorption amount. However, as described above, the pressure sensitivity also increases with an increase in the amount of sensitizing dye. Moreover, due to their shape, tabular grains are more apt to deform as a result of the application of external forces, and satisfactory embodiments have not been achieved using methods such as those described above.

Furthermore, a method of reducing pressure blackening by adding polyhydroxybenzene to tabular grains has been disclosed in JP-A-64-72141, but the photographic speed is reduced with this method, the pressure blackening is not improved to a satisfactory level in cases where a high photographic speed is required.

SUMMARY OF THE INVENTION

An object of the present invention is to improve, to the extent that the above described problems are not encountered in practical applications, the pressure sensitivity of a photosensitive silver halide emulsion comprising tabular grains which has been optimally chemically sensitized.

The above described object is achieved by providing a silver halide photographic photosensitive material comprising a support, having thereon at least one hydrophilic colloid layer, at least one layer of which is a photosensitive silver halide emulsion layer comprising tabular silver halide grains having an aspect ratio of at least 3, said photosensitive silver halide emulsion layer being prepared by reacting a water soluble silver salt with a water soluble alkali halide to form an emulsion comprising tabular silver halide grains, de-salting the thus formed emulsion, chemically sensitizing the emulsion and coating the resulting chemically sensitized emulsion comprising tabular silver halide grains onto the support, wherein an inorganic salt comprising a typical element or an ion composed thereof, and chlorine, i.e., a chloride of an element or ion selected from the group consisting of Na, K, Mg, Ca, Li and NH_4^+ is added to said emulsion either immediately after de-salting, after de-salting but prior to chemical sensitization, during chemical sensitization, after chemical sensitization but prior to coating, or immediately prior to coating.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is described in detail below.

The manufacturing process for a silver halide emulsion can be broadly divided, for example, into the processes of grain formation, de-salting, chemical sensitization and coating. The grain formation stage can be further divided, for example, into the stages of nuclei formation, ripening, and grain growth. The manufacturing process for a silver halide emulsion as described above may be modified. For example, the order in which the processes is carried but may be reversed, or the individual processes may be carried out repeatedly.

In this regard, methods for improving the pressure characteristics comprising adding an inorganic compound containing chlorine during grain formation, and establishing a silver halochloride layer constituting the thus treated grains are disclosed in JP-A-1-102547 and JP-A-1-102548. The present invention is fundamentally different from the above cited patent publications in that an inorganic salt comprising chlorine and a typical element or an ion composed thereof is added after grain formation.

Examples of the inorganic salt comprising chlorine and a typical element or an ion composed thereof for use in the present invention include 1) sodium chloride, 2) potassium chloride, 3) calcium chloride, 4) magnesium chloride, 5) lithium chloride and 6) ammonium chloride, but the inorganic salts are not limited to these examples.

Furthermore, the addition of inorganic salts of transition metals such as Rh, Pd and Ir, for example, is well known in the industry. The transition metals have a major effect on the photographic properties, but the effect is fundamentally different from that of the present invention.

In this way, inorganic salt comprising chlorine and a typical element or an ion composed thereof used in the present invention does not include the inorganic salts of transition metals.

The inorganic salt comprising chlorine and a typical element or an ion composed thereof of the present invention, i.e., chloride of the present invention is added at least once immediately after the desalting process following grain formation, after desalting but prior to chemical sensitization, during chemical sensitization, after chemical sensitization but prior to coating or immediately before coating, preferably after de-salting but prior to chemical sensitization or after chemical sensitization but prior to coating or immediately before coating, and most desirably after de-salting but prior to chemical sensitization.

The addition amount of the chloride of the present invention is from 5 to 200 mmol, and preferably from 10 to 100 mmol, per mol of silver contained in the silver halide emulsion.

The tabular silver halide grains of this present invention are preferably subjected to reduction sensitization.

The reduction sensitization in the present invention may be carried out during nuclei formation which is the first stage of grain formation, during physical ripening or during grain growth. The reduction sensitization may also be carried out before chemical sensitization or following chemical sensitization.

In cases where the emulsion is subjected to both gold sensitization and reduction sensitization, the reduction sensitization is preferably carried out before chemical sensitization so that no undesirable fogging is produced.

Methods in which reduction sensitization is carried out during the growth of the silver halide grains is most desirable. Here, the term "during growth" includes methods wherein reduction sensitization is carried out during the physical ripening of the silver halide grains or when the silver halide grains are still being grown by adding a water soluble silver salt and a water soluble alkali halide, and methods wherein reduction sensitization is carried out after temporarily stopping growth during the growth operation and then resuming the growing operation.

The reduction sensitization for use in the present invention can be carried out using methods selected from among those in which a known reducing agent is added to the silver halide emulsion, those methods in which growth or ripening is carried out in a low pAg environment of pAg from 1 to 7, known as silver ripening, and those methods in which growth or ripening is carried out under high pH conditions at a pH of from 8 to 11, known as high pH ripening. Furthermore, two or more reduction sensitization methods may be used in combination.

The method in which reduction sensitizing agents are added is preferred from the point of view to control of the level of reduction sensitization.

Known reduction sensitizing agents for use in the present invention include stannous salts, amines and polyamines, hydrazine derivatives, formamidinesulfinic acid, silane compounds, ascorbic acid compounds and borane compounds, for example. Two or more of the sensitizing agents may be used in combination. Ascorbic acid, thiourea dioxide and dimethylaminoborane are preferred as reduction sensitizing agents. The addition amount of the reduction sensitizing agent varies depending on the emulsion preparation conditions, but an addition amount within the range of from 10^{-8} to 10^{-3} mol per mol of silver halide contained in the emulsion is generally employed, and an amount within the range of from 10^{-7} to 10^{-5} mol per mol of silver halide is preferred.

The reduction sensitizing agent can be dissolved in alcohols, glycols, ketones, esters, amides etc. and added during grain formation or before or after chemical sensitization. The addition can be made at any stage during the preparation of the emulsion, but the reduction sensitizing agent is preferably added during grain growth and/or after grain formation and prior to chemical sensitization. In those cases where the sensitizing agent is added during grain growth, the sensitizing agent can be added to the reaction vessel prior to the addition of a soluble silver salt and alkali halide, but addition at an appropriate stage of grain formation, i.e., during grain formation and/or immediately after grain formation is more desirable. Furthermore, a reduction sensitizing agent can be added to either the water soluble silver salt or water soluble alkali halide solution prior to introduction into the reaction vessel, to thereby carry out grain formation. Furthermore, a solution of the reduction sensitizing agent may be divided into portions and added on several occasions as grain formation proceeds, or the solution of the reduction sensitizing agent is preferably added continuously over a long period of time.

In the present invention, the combined use of a thiosulfonic acid compound as disclosed in Japanese Patent Applications 63-159888 and 63-258787 together with a reduction sensitizing agent is preferred.

Known sulfur sensitizing agents can be used in the present invention. For example, useful sulfur sensitizing agents include thiosulfate, allylthiocarbamidothiourea, allylisothiocyanate, cystine, p-toluenethiosulfonate and rhodanine, etc. Use can also be made of the sulfur sensitizing agents disclosed, for example, in U.S. Patents 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313 and 3,656,955, West

German Patent 1,422,869, JP-B-56-24937 and JP-A-55-45016. The addition amount of the sulfur sensitizing agent is that amount which is sufficient to effectively increase the photographic speed of the emulsion. The addition amount varies depending on various conditions, such as the amount of hydroxyazaindene added, the pH, the temperature and the size of the silver halide grains, but generally, an addition amount of the sulfur sensitizing agent of from about 10^{-5} mol to about 10^{-1} mol per mol of silver halide is preferred.

Selenium sensitization can be used in place of sulfur sensitization in the present invention. Aliphatic isoselenocyanates such as allylisoselenocyanate, selenoureas, selenoketones, selenoamides, selenocarboxylic acids and esters, selenophosphates and selenides such as diethylselenide and diethyldiselenide, for example, can be used as the selenium sensitizing agent, and actual examples thereof are disclosed in U.S. Patents 1,574,944, 1,602,592 and 1,623,499.

The addition amount of the selenium sensitizing agent varies over a wide range in the same way as with the sulfur sensitizing agent, but generally, an addition amount of from about 10^{-9} mol to about 10^{-6} mol per mol of silver halide is preferred.

Various gold compounds in which the oxidation number of the gold is +1 or +3 can be used as the gold sensitizing agent for use in the present invention. Useful examples include chloroauric acid salts, potassium chloroaurate, auric trichloride, potassium auric thiocyanate, potassium rhodoaurate, tetracyanoauricamide, ammonium aurothiocyanate and pyridyltrichlorogold.

In those cases where gold sensitization is carried out together with sulfur sensitization or selenium sensitization, gold nuclei and silver sulfide gold nuclei or silver selenide gold nuclei are formed as sensitization nuclei, and the number of these nuclei and the composition of the silver sulfide gold nuclei or silver selenide gold nuclei have an important effect on the electron trapping properties and/or the development properties. Namely, the proportion of gold sensitizing agent with respect to the sulfur sensitizing agent or selenium sensitizing agent has a pronounced effect on the photographic speed of the emulsion. Thus, depending on the ripening conditions, the proportion of sensitizing agents is selected to provide the desired photographic speed of the emulsion.

The proportion in which the sulfur sensitizing agent or selenium sensitizing agent and the gold sensitizing agent are added is preferably such that the ratio of the number of gold atoms to the number of sulfur atoms which of the sulfur sensitizing agent form silver sulfide or the number of selenium atoms which of the selenium sensitizing agent form silver selenide is from 1/2 to 1/200.

The gold sensitizing agent may be added at the same that the sulfur sensitizing agent or selenium sensitizing agent is added, or during the course of sulfur or selenium sensitization or after the completion of sulfur or selenium sensitization.

A preferred effect of the present invention is obtained when two or more sensitizing dyes are used conjointly.

The addition of the sensitizing dyes may be made at any time during the manufacturing process for a silver halide emulsion as described above, but addition thereof at the time of chemical sensitization is especially desirable for obtaining high photographic speed.

Cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, styryl dyes, hemi-cyanine dyes, oxonol dyes and hemi-oxonol dyes, for example, can be used as sensitizing dyes in the present invention.

Useful sensitizing dyes include these disclosed, for example, in U.S. Patents 3,522,052, 3,619,197, 3,713,828, 3,615,643, 3,615,632, 3,617,293, 3,628,964, 3,703,377, 3,666,480, 3,667,960, 3,679,428, 3,672,897, 3,769,026, 3,556,800, 3,615,613, 3,615,638, 3,615,635, 3,705,809, 3,632,349, 3,677,765, 3,770,449, 3,770,440, 3,769,025, 3,745,014, 3,713,828, 3,567,458, 3,625,698, 2,526,632 and 2,503,776, JP-A-48-76525 and Belgium Patent 691,807.

The addition amount of the sensitizing dye is at least 80%, and preferably at least 100% but not more than 200%, of the amount for saturated adsorption of the silver halide grains. The addition amount is generally at least 300 mg but less than 1500 mg, and preferably at least 400 mg but less than 1000 mg, per mol of silver halide.

Moreover, the amount at saturation adsorption is the value determined by centrifuging the emulsion in a centrifuge and measuring the dye absorption of the supernatant liquid.

Actual non-limiting examples of sensitizing dyes which are effective in the present invention are indicated below.

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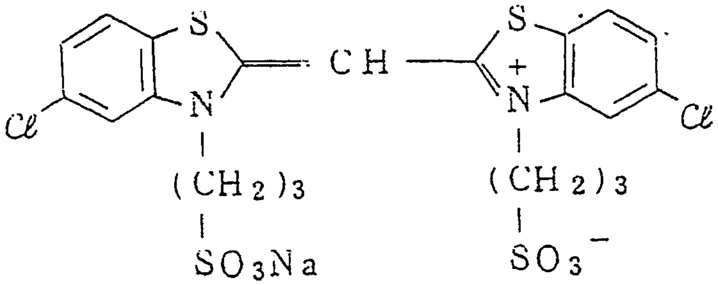

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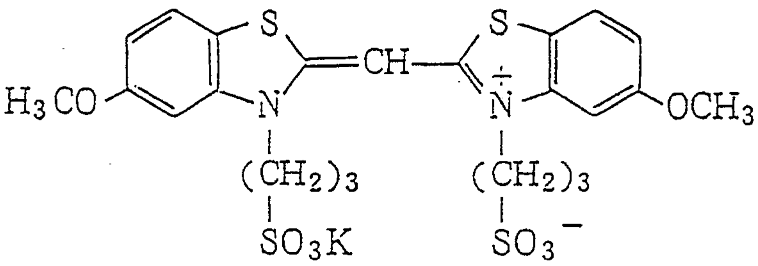

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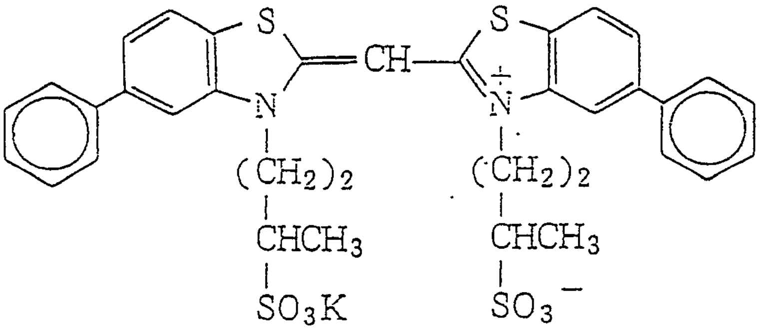

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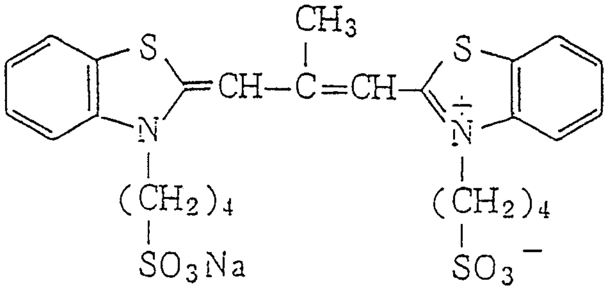

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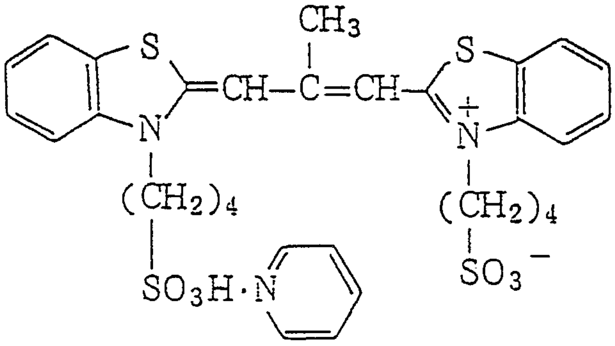

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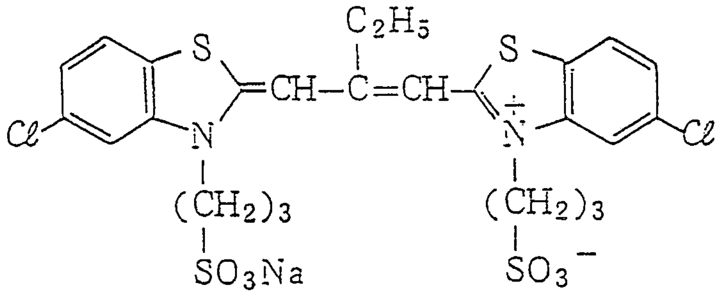

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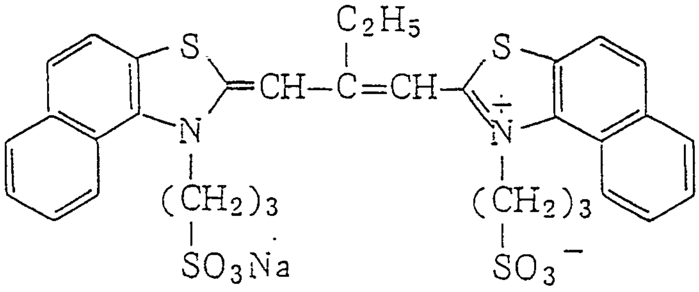

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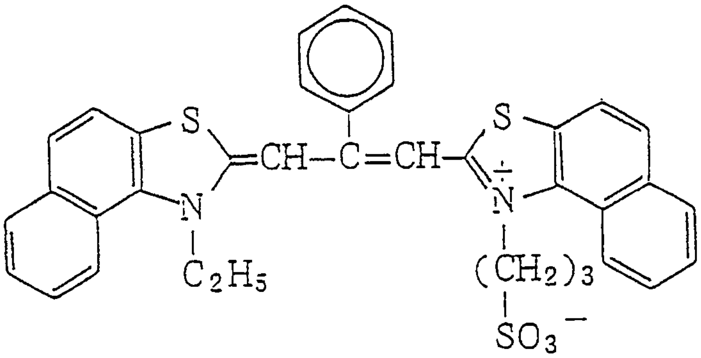

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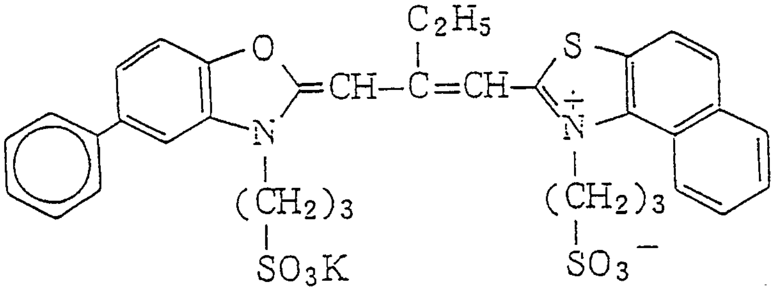

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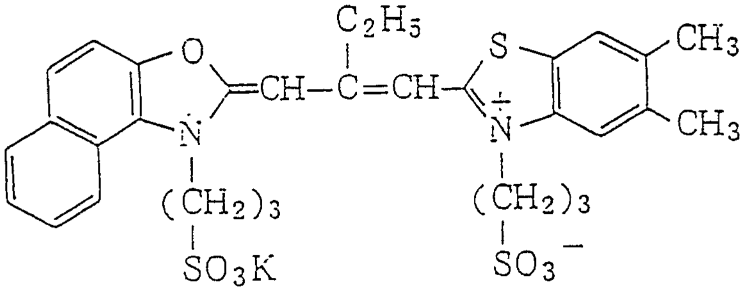

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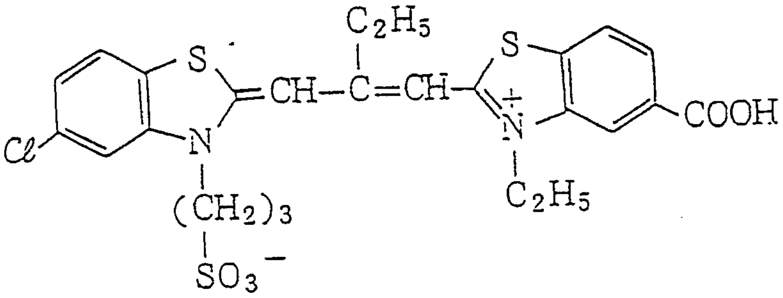

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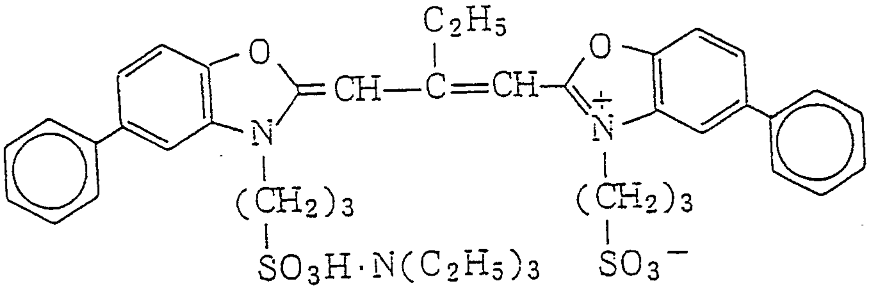

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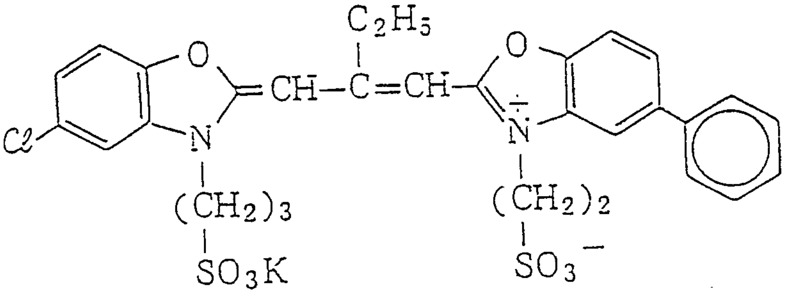

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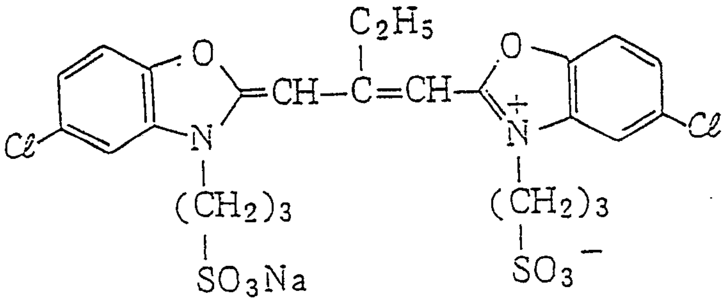
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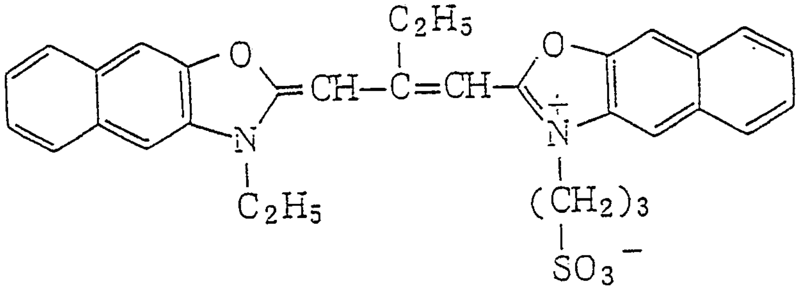
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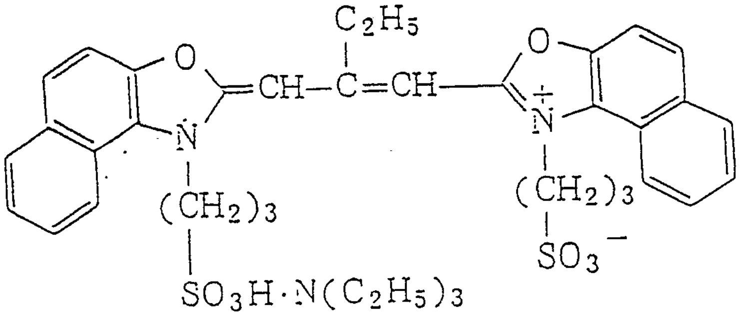
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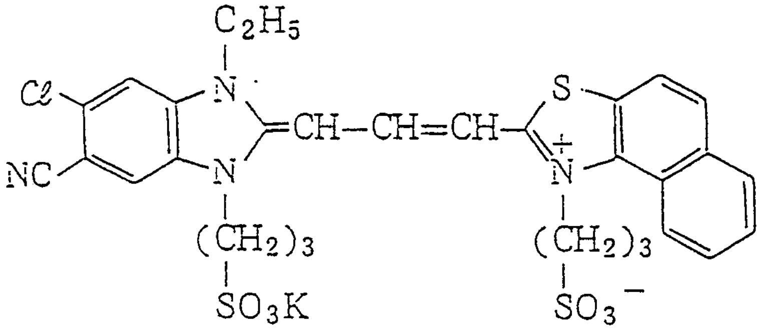

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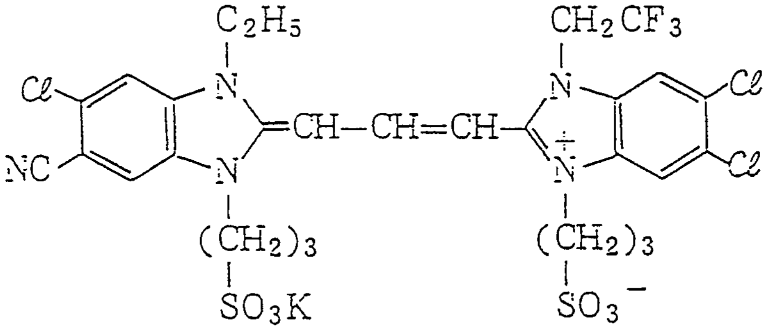

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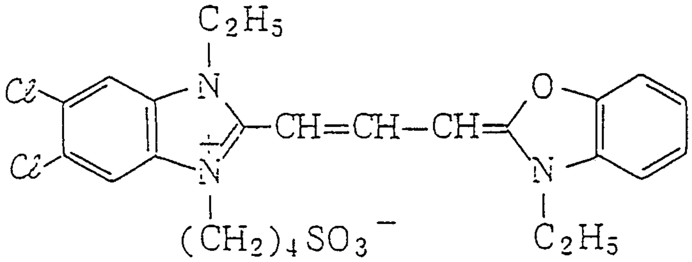

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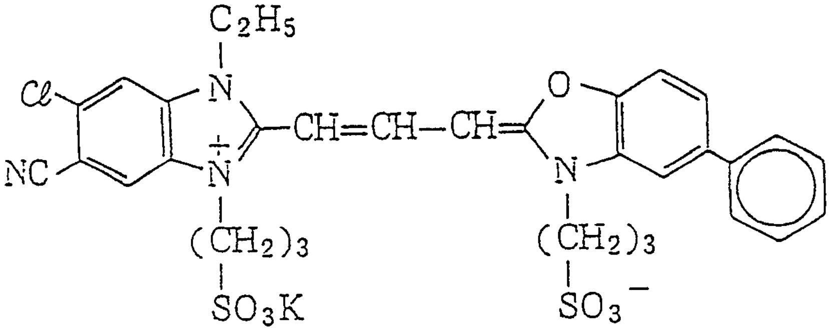
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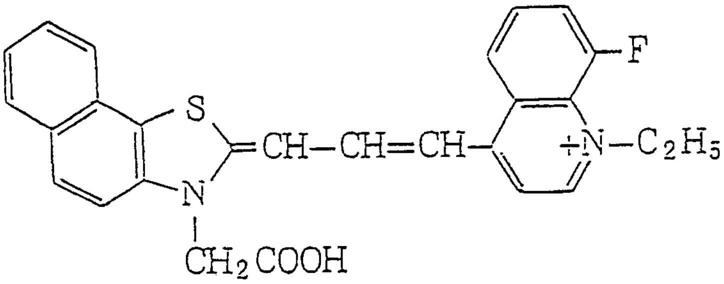
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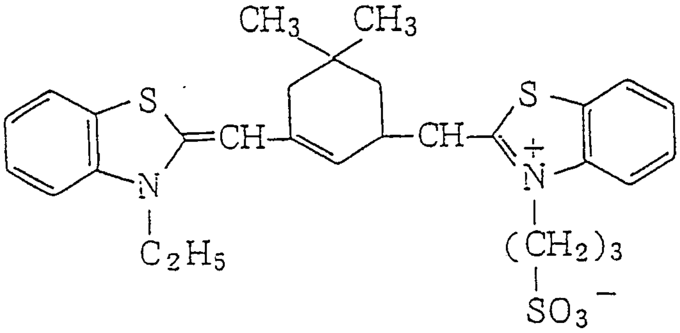
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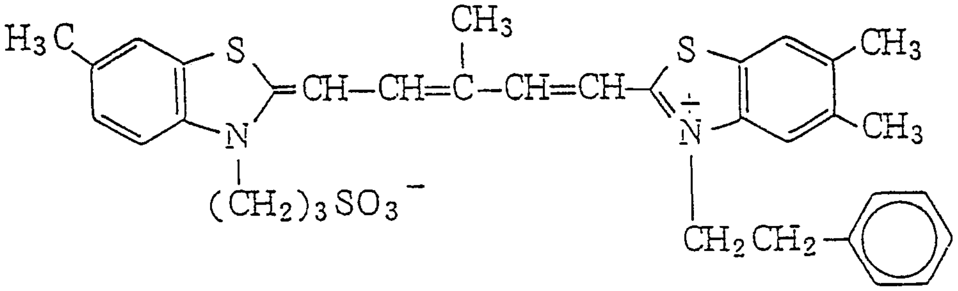

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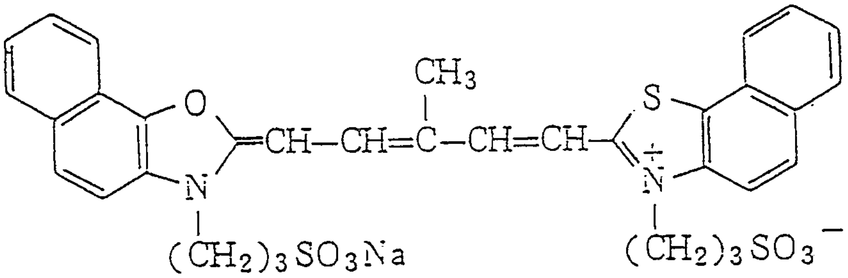

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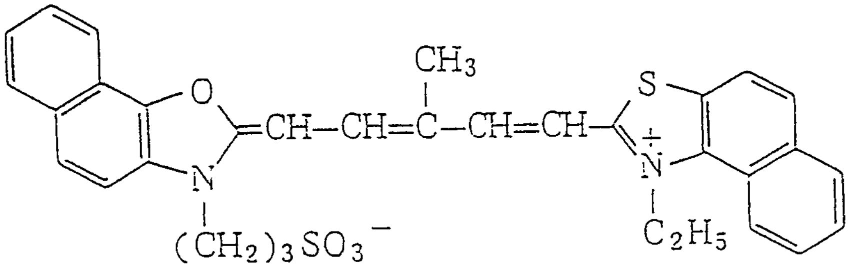

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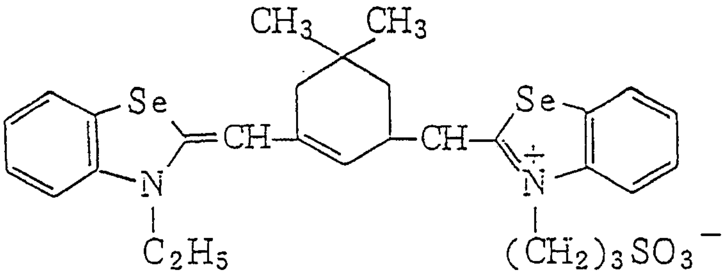

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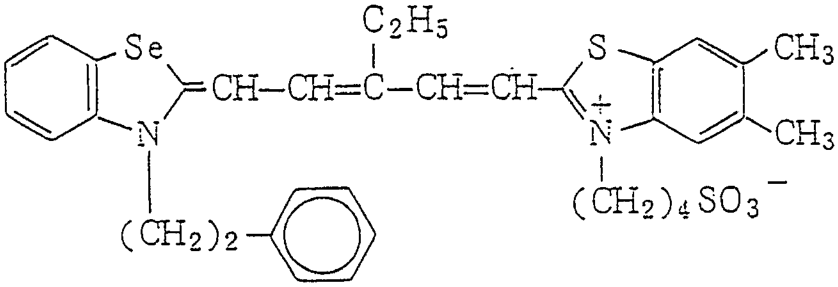

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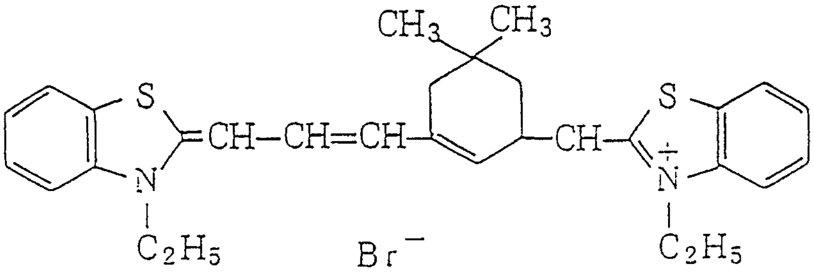

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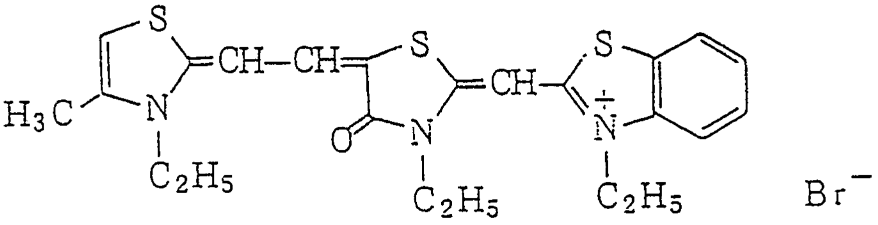
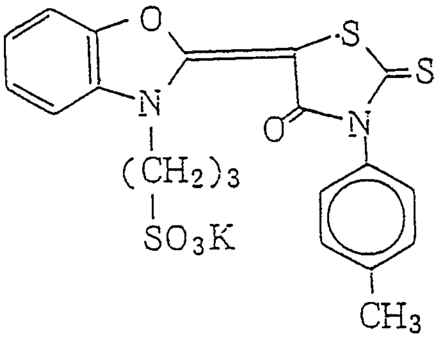
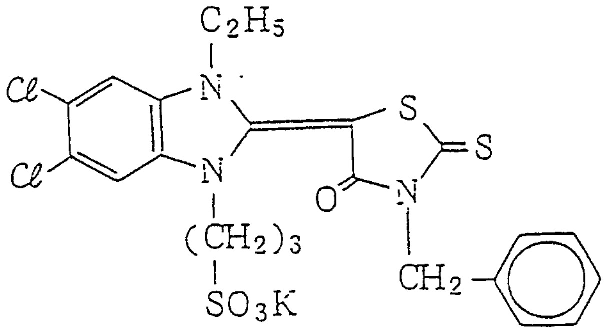

S
CH
CH
S
CH
S
H3C
N
O
N
N
C2H5
C2H5
C2H5
Br⁻

(30)


O
S
S
N
O
N
(CH2)3
SO3K
CH3

(31)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S
S
Cl
N
O
N
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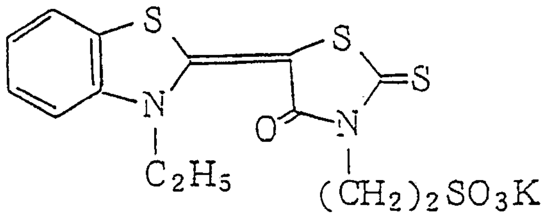
(32)



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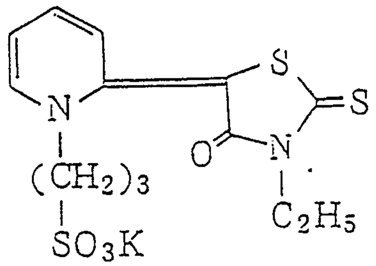

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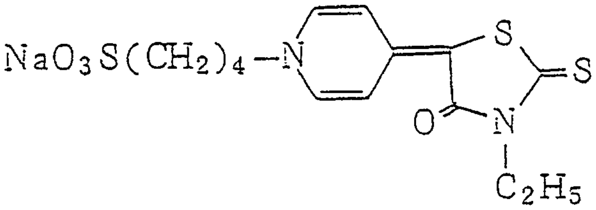

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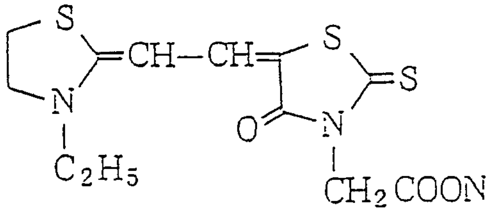

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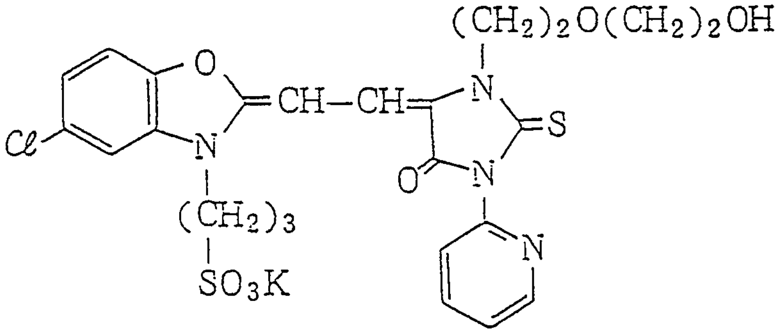
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O
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N
S
Cl
N
O
N
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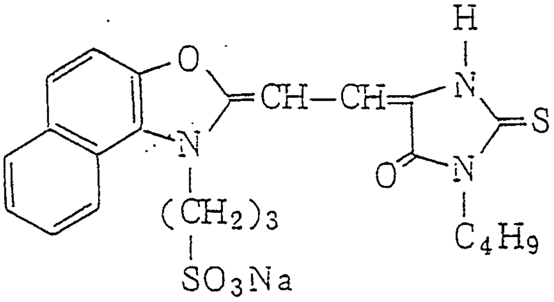
SO3K
N

(37)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O
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N
S
N
O
N
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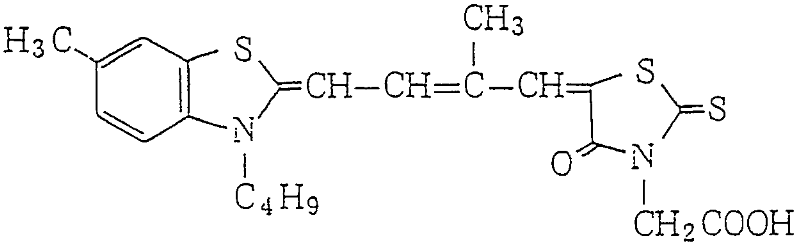
C4H9
SO3Na

(38)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H3C
S
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S
S
N
O
N
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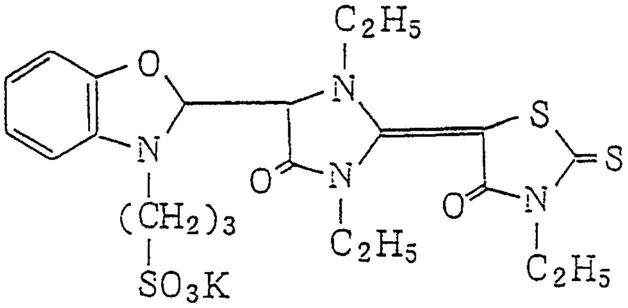
(39)



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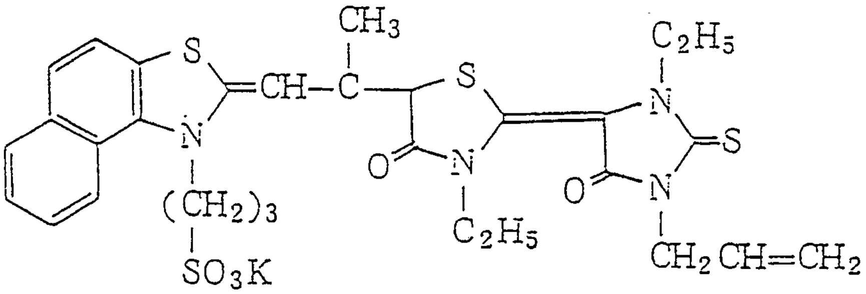

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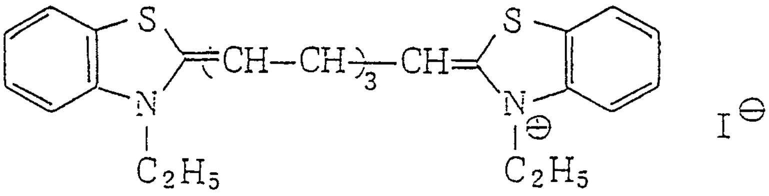

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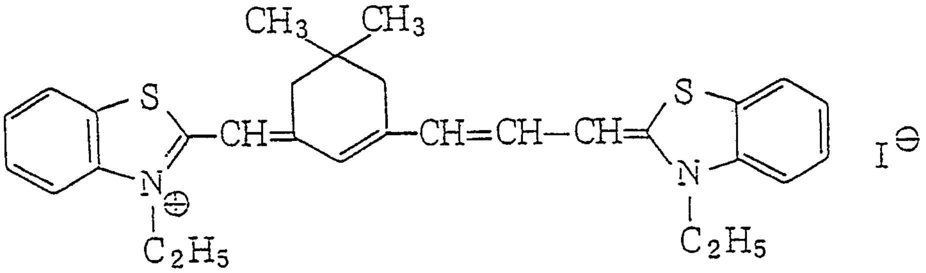

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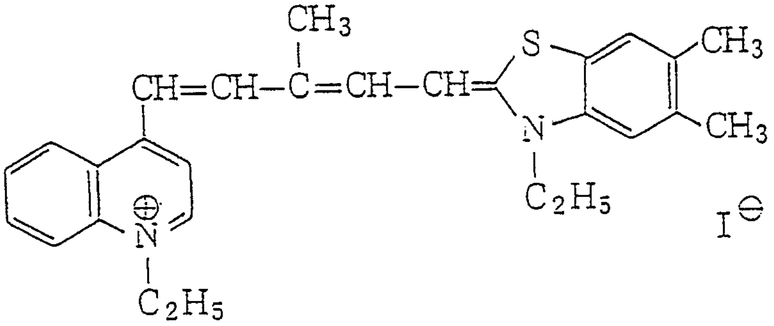


The cyanine dyes among the above described dyes are especially desirable.

The tabular silver halide grains of the present invention are described below.

Tabular silver halide emulsions are readily prepared easily with reference to the methods described, for example, by Cugnac and Chateau in "Evolution of the Morphology of Silver Bromide Crystals during Physical Ripening", Science et Industrie Photographique, volume 33, No. 2 (1962), pages 121-125, by Duffin in Photographic Emulsion Chemistry (Focal Press, New York, 1966), pages 66-72, by A.P.H. Trivelli and W.F. Smith in Photographic Journal, volume 80, page 285 (1940), and the methods disclosed in JP-A-58-127921, JP-A-58-113927, JP-A-58-113928 and U.S. Patent 4,439,520.

Furthermore, tabular grain emulsions can be obtained by forming seed crystals of which tabular grains account for at least 40% by weight under conditions of a comparatively low pBr value of not more than 1.3, and then growing the seed crystals by adding soluble silver and halide salt solutions simultaneously while maintaining a pBr value of about the same order.

The soluble silver and halide salt solutions are preferably added in such a way that no new crystal nuclei are formed during the grain growth process.

The size of the tabular silver halide grains can be controlled, for example, by adjusting the temperature, selecting the type and amount of solvent, and by controlling the rate of addition of the silver salt and the halide solutions which are used during the grain growth.

Moreover, from among the tabular silver halide grains, mono-disperse hexagonal tabular grains are especially useful.

Details of the structure and method of preparation of the grains referred to herein as monodisperse hexagonal tabular grains are provided in Japanese Patent Application 61-299155. The above noted emulsions are silver halide emulsions comprising a dispersion medium and silver halide grains in which at least 70% of the total projected area of the silver halide grains is accounted for by tabular silver halide grains having a hexagonal form, the ratio of the length of the longest side with respect to the length of the shortest side of the tabular grains is not more than 2 and which tabular grains have two parallel planes as external surfaces. Moreover, the tabular grains having a hexagonal form are monodispersed grains such that the variation coefficient of the grain size distribution (the value obtained by dividing the standard deviation of the grain size expressed as the diameter of the circles calculated from the projected areas by the average grain size) is not more than 20%. The crystal structure may be uniform, but crystals wherein the interior and exterior parts have a different halogen composition are preferred, and the grains may have a layer-like structure. Furthermore, reduction sensitization nuclei are preferably included within the grains.

The tabular grains of the present invention are such that the mean aspect ratio of at least 50% of the grains accounting for the total projected area of the silver halide grains is at least 3.0, and the aspect ratio for all of the grains of thickness not more than 0.3 μm is preferably at least 3, and most desirably at least 5 and not more than 10.

The average projected area diameter of the tabular grains of the present invention is from 0.3 to 2.0 μm, and most desirably from 0.5 to 1.6 μm. Furthermore, the distance between the parallel planes (the thickness of the grains) is from 0.05 to 0.3 μm, and most desirably from 0.1 to 0.25 μm.

Halogen exchange type grains (conversion type grains) such as those disclosed in British Patent 635,841 and U.S. Patent 3,622,318 can be used to particular advantage in the present invention.

Silver halide emulsions of higher photographic speed can be obtained by subjecting the surfaces of the tabular silver halide grains of the present invention to conversion.

The addition of an aqueous halogen solution having a lower solubility product with silver than the halogen composition of the grain surface before halogen exchange is generally used as a method of conversion. For example, an aqueous solution of potassium bromide and/or potassium iodide is added in the case of silver chloride or silver chlorobromide tabular grains, an aqueous solution of potassium iodide is added in the case of silver bromide or silver iodobromide tabular grains, to thereby carry out conversion. A lower concentration of the aqueous solution added to the emulsion is desirable, and the concentration is preferably not more than 30 wt%, and more preferably not more than 10 wt%. Moreover, the exchange halogen solution is preferably added at a rate of not more than 1 mol% per minute per mol of silver halide before halogen conversion. Moreover, sensitizing dyes may be present at the time of halogen exchange, or a fine grain silver halide, including silver bromide, silver iodobromide or silver iodide, can be added instead of the aqueous solution of the exchange halogen. The size of the fine grains is not more than 0.2 μm, preferably not more than 0.1 μm, and most desirably not more than 0.05 μm. The amount of halogen exchange is preferably from 0.1 to 1 mol%, and most desirably from 0.1 to 0.6 mol%, of the silver halide prior to exchange.

The method of halogen conversion of the present invention is not limited to any one of the methods indicated above, and these methods can be used in combination according to the intended purpose. An iodide content of not more than 3 mol% is desirable for the silver halide composition of the grain surface before halogen exchange, and a surface iodide content of not more than 1.0 mol% is especially desirable.

The methods in which a silver halide solvent is present are especially effective when carrying out halogen exchange as described above. Thioether compounds, thiocyanate, ammonia and tetra-substituted thiourea are preferred solvents. From among these, the thioether compounds and thiocyanate are especially effective, and the use of from 0.5 to 5 grams of thiocyanate of from 0.2 to 3 grams of thioether per mol of silver halide is desirable.

Furthermore, compounds which release inhibitors during development, such as those disclosed in JP-A-61-230135and Japanese Patent Application 61-169499 can be added to the emulsion of the present invention.

Cadmium salts, zinc salts, lead salts, thallium salts, iridium salts or complex salts thereof, rhodium salts or complex salts thereof and iron salts or complex salts thereof, for example, may be present during the grain formation or physical ripening processes for preparing the silver halide grains of the present invention.

Furthermore, silver halide solvents such as thiocyanate, ammonia, thioether compounds, thiazolidinethione, and tetra-substituted thiourea, for example, may also be present during grain formation. Of these, thiocyanate, ammonia and thioether are preferred as solvents in the present invention.

The apex development initiation type grains disclosed in Japanese Patent Application 62-141112 are very useful as the tabular grains for use in this present invention.

Various compounds can be included in the photographic emulsion of the present invention for preventing the occurrence of fogging during the manufacture, storage or photographic processing of the photosensitive material or for stabilizing the photographic performance. Namely, many compounds which are known as anti-foggantsor stabilizers, such as azoles (for example, benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, nitroindazoles, benzotriazoles, aminotriazoles); mercapto compounds (for example, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, mercaptotetrazoles, mercaptopyrimidines, mercaptotriazines); thioketo compounds such as oxazolinethione; azaindenes [for example, triazaindenes, tetraazaindenes (especially 4-hydroxy substituted (1,3,3a,7)-tetraazaindenes), pentaazaindenes]; benzenethiosulfonic acid; benzenesulfinic acid and benzenesulfonic acid amide, for example, can be added.

The use of the nitrogen containing compounds and derivatives thereof disclosed in JP-A-60-76743 and JP-A-60-87322, the mercapto compounds disclosed in JP-A-60-80839, the heterocyclic compounds disclosed in JP-A-57-164735, and the heterocyclic compounds and silver complex salts (for example, silver 1-phenyl-5-mercaptotetrazole), for example, is especially desirable.

Various surfactants can be included in the photographic emulsion layers or other hydrophilic colloid layers of the photosensitive material of the present invention, for example, as coating promotors, as antistatic agents, for improving slip properties, for emulsification and dispersion, for preventing sticking, or for improving photographic performance (for example, for accelerating development, film hardening or for increasing sensitivity).

For example, use can be made of non-ionic surfactants, such as saponin (steroid based), alkylene oxide derivatives (for example, polyethylene glycol, polyethylene glycol/polypropylene glycol condensate, polyethylene glycol alkyl ethers or polyethylene glycol alkyl aryl ethers and poly(ethylene oxide) adducts of silicones); anionic surfactants such as alkylsulfonates, alkylbenzenesulfonates, alkylnaphthalenesulfonates, alkylsulfate esters, N-acyl-N-alkyltaurines, sulfosuccinate esters, and sulfoalkylpolyoxyethylene alkylphenyl ethers; amphoteric surfactants, such as alkylbetaines and alkylsulfobetaines; and cationic surfactants such as aliphatic and aromatic quaternary ammonium salts, pyridinium salts and imidazolium salts, for example.

From among the above noted surfactants the use of saponin, anionic surfactants such as sodium tetradecylbenzenesulfonate, sodium di-2-ethylhexyl-α-sulfosuccinate, sodium p-octylphenoxyethoxyethanesulfonate, sodium dodecylsulfate, sodium triisopropylnaphthalenesulfonate,sodium and sodium N-methyl-oleoyltaurine, cationic surfactants such as dodecyltrimethylammonium chloride, N-oleoyl-N',N',N'-trimehylammoniodiaminopropane bromide and dodecylpyridinium chloride, betaines such as N-dodecyl-N,N-dimethylcarboxybetaine, and N-oleyl-N,N-dimethylsulfobutylbetaine, and non-ionic surfactants such as poly(average degree of polymerization(n = 10)oxyethylene cetyl ether, poly(n = 25)oxyethylene p-nonylphenyl ether and bis(1-poly(n = 15)oxyethyleneoxy-2,4-di-tert-phenyl)ethane, for example, is especially desirable.

The use of fluorine containing surfactants, such as potassium perfluoro-octanesulfonate, sodium salt of N-propyl-N-perfluoro-octanesulfonylglycine, sodium salt of N-propyl-N-perfluoro-octanesulfonylaminoethyloxypoly(n = 3)oxyethylenebutanesulfonic acid, N-perfluoro-octanesulfonyl-N' ,N' ,N' -trimethylammoniodiaminopropane chloride, N-perfluoro-decanoylaminopropyl-N' ,N'-dimethyl-N'-carboxybetaine, the non-ionic surfactants disclosed, for example, in JP-A-60-80848, JP-A-61-112144, and Japanese Patent Applications 61-13398 and 61-16056, alkali metal nitrates, electrically conductive tin oxide, zinc oxide, vanadium pentoxide or complex oxides wherein these have been doped with antimony, for example, as an anti-static agent is desirable.

As disclosed in U.S. Patents 2,992,101, 2,701,245, 4,142,894 and 4,396,706, fine particles of homopolymers of poly(methyl methacrylate) or copolymers of methyl methacrylate and methacrylic acid, organic compounds such as starch, and inorganic compounds such as silica, titanium dioxide and strontium barium sulfate, for example, can be used as a matting agent in the present invention.

The particle size of tee matting agent is preferably from 1.0 to 10 μm, and most desirably from 2 to 5 μm.

The silicone compounds disclosed in U.S. Patents 3,489,576 and 4,047,958, the colloidal silica disclosed in JP-B-56-23139, and also paraffin wax, higher fatty acid esters and starch derivatives, for example, can be used as a slip agent in the surface layer of the photographic photosensitive material of the present invention.

Polyols, such as trimethylolpropane, pentanediol, butanediol, ethylene glycol and glycerine, for example, can be used as a plasticizer in the hydrophilic colloid layers of the photographic photosensitive material of the present invention.

Gelatin and other hydrophilic colloids can be used as the binder or protective colloid which for use in the emulsion layers, intermediate layers and surface protective layers of the photosensitive material of the present invention.

For example, the binder material of the present invention can comprise proteins such as gelatin derivatives, graft polymers of gelatin and other polymers, albumin and casein; cellulose derivative such as hydroxyethylcellulose, carboxymethylcellulose and cellulose sulfate esters, sodium alginate, sugar derivatives such as starch derivatives, and various synthetic hydrophilic macromolecular substances such as homopolymers such as poly(vinyl alcohol), partially acetalated poly(vinyl alcohol), poly(N-vinylpyrrolidone), poly(acrylic acid), poly(methacrylic acid), polyacrylamide, polyvinylimidazole and polyvinylpyrazole, for example, and copolymers of these materials.

As well as lime treated gelatin, acid treated gelatin and enzyme treated gelatin can be used as the gelatin, and gelatin hydrolyzates and enzyme degraded gelatins can also be used.

From among the above described materials the combined use of gelatin together with dextran and/or polyacrylamide of average molecular weight of from 5000 to 100,000 as the binder material is preferred. The methods disclosed in Japanese Patent Applications 61-213503and 61-298405 are also effective in the present invention.

Inorganic or organic film hardening agents may be included in the photographic emulsions and non-photosensitive hydrophilic colloids of the present invention. For example, use can be made of chromium salts (for example, chrome alum), aldehydes (for example, formaldehyde, glutaraldehyde), N-methylol compounds (for example, dimethylolurea), dioxane derivatives (for example, 2,3-dihydroxydioxane), active vinyl compounds (for example, 1,3,5-triacryloyl-hexahydro-s-triazine, bis(vinylsulfonyl)methyl ether, N,N'-methylene-bis[β-(vinylsulfonyl)propionamide]), active halogen compounds (for example, 2,4-dichloro-6-hydroxy-s-triazine), mucohalogen acids (for example, mucochloric acid), iso-oxazoles, dialdehyde starch, and 2-chloro-6-hydroxytriazinylatedgelatin, these compounds being used either individually or in combinations. From among the above described compounds, the active vinyl compounds disclosed in JP-A-53-41221, JP-A-53-57257, JP-A-59-162546 and JP-A-60-80846 and the active halogen compounds disclosed in U.S. Patent 3,325,287 are preferred.

N-carbamoylpyridinium salts (for example, (1-morpholinocarbonyl-3-pyridinio)methanesulfonate), and haloamidinium salts (for example, 1-(1-chloro-1-pyridinomethylene)pyrrolidinium-2-naphthalenesulfonate) are also useful.

Polymeric film hardening agents can also be used effectively as a film hardening agent of the present invention.

Examples of polymeric film hardening agents for use in the present invention include dialdehyde starch, polyacrolein, polymers having aldehyde groups such as the acrolein copolymers disclosed in U.S. Patent 3,396,029, polymers having epoxy groups as disclosed in U.S. Patent 3,623,878, polymers having dichlorotriazine groups as disclosed, for example, in U.S. Patent 3,362,827 and Research Disclosure, 17333 (1978), polymers having active ester groups as disclosed in JP-A-56-66841, and polymers having an active vinyl group or precursor group thereof as disclosed, for example, in JP-A-56-142524, U.S. Patent 4,161,407, JP-A-54-65033 and Research Disclosure, 16725 (1978). Polymers having an active vinyl group or precursor group thereof are preferred, and from among the polymers having an vinyl group, or precursor group thereof, those polymers having an active vinyl group or precursor thereof which are bonded to the main chain by a long spacer, such as those disclosed in JP-A-56-142524, are especially desirable.

Poly(ethylene terephthalate) films or cellulose triacetate films are preferred as the support for use in the present invention.

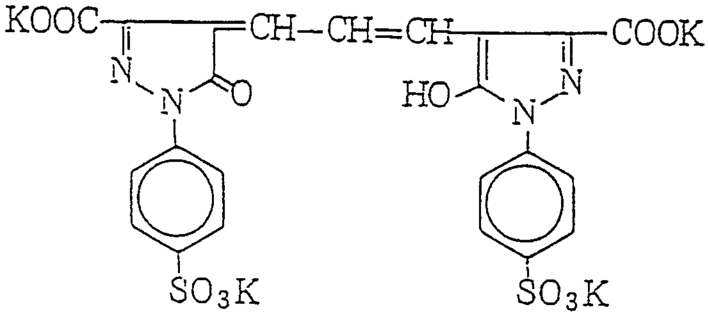
The surface of the support is preferably subjected to a corona discharge treatment or a glow discharge treatment or an ultraviolet irradiation treatment in order to improve the adhesion of the hydrophilic colloid layer. Alternatively, an under-layer comprising of a styrene/butadiene based latex or a vinylidene chloride based latex, for example, may be established on the support, and a gelatin layer may also be established over this under-layer.

Furthermore, an under-layer comprising an organic solvent containing a polyethylene swelling agent and gelatin may be provided on the support. The adhesion with the hydrophilic colloid layer can be further improved by subjecting the under-layer to surface treatment.

The silver halide photographic photosensitive material of the present invention may comprise photographic emulsion layers or other layers which are colored with dyes for absorbing light in the long wavelength band to prevent the occurrence of halation or irradiation, or to control the spectral composition of the light incident on the photographic emulsion layer by providing a filter layer. A layer for preventing the occurrence of crossover may be established below the photographic emulsion layers in the case of double sided films such as X-ray films for direct medical applications. Useful colored dyes include oxonol dyes which have a pyrazolone nucleus or a barbituric acid nucleus, azo dyes, azomethine dyes, anthraquinone dyes, arylidene dyes, styryl dyes, triarylmethane dyes, merocyanine dyes and cyanine dyes.

Typical colored dyes for use in the present invention are indicated below, but the present invention is not limited to these dyes.

(a)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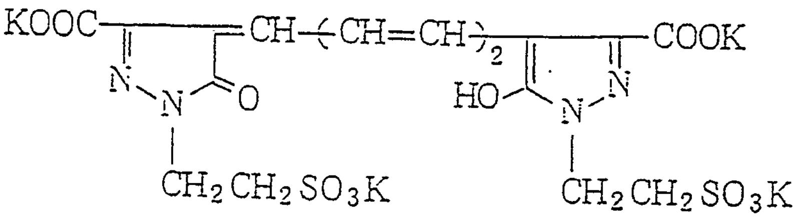
(b)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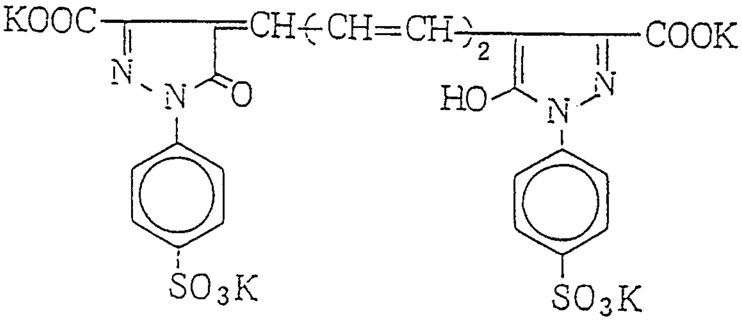
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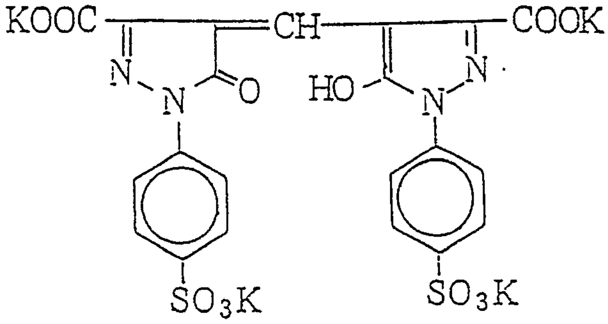
(d)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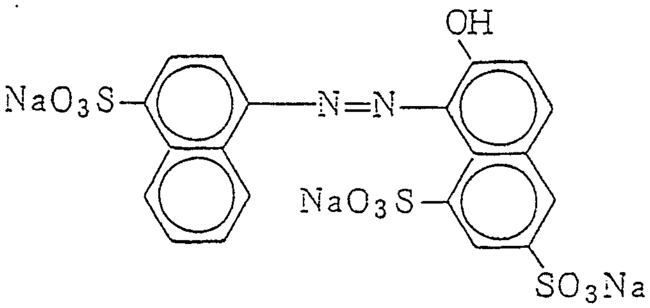
(e)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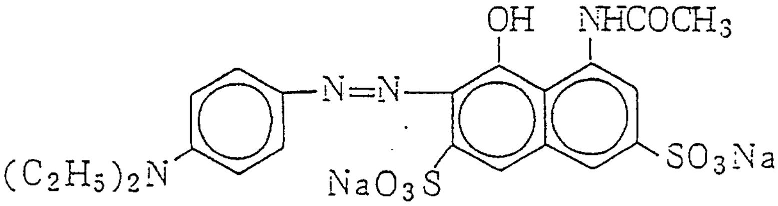
(f)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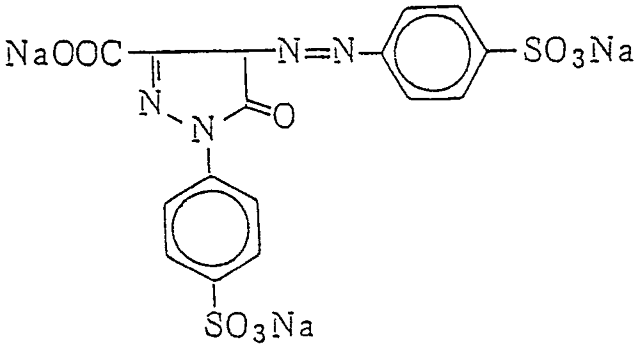
(g)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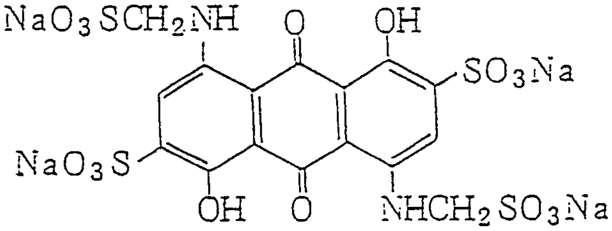
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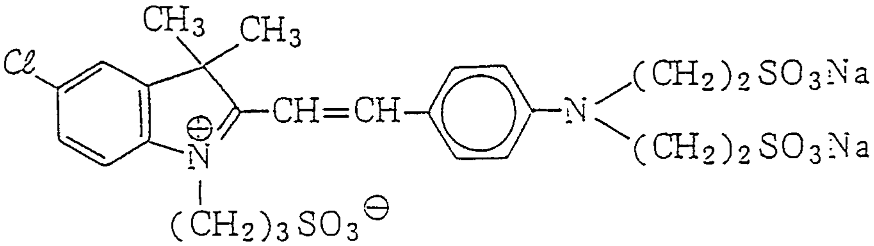
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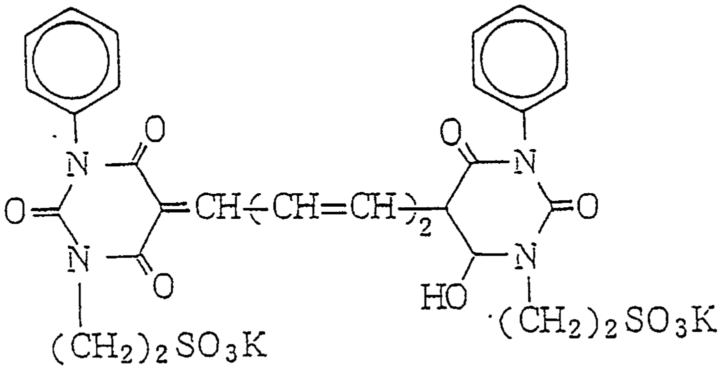
(j)



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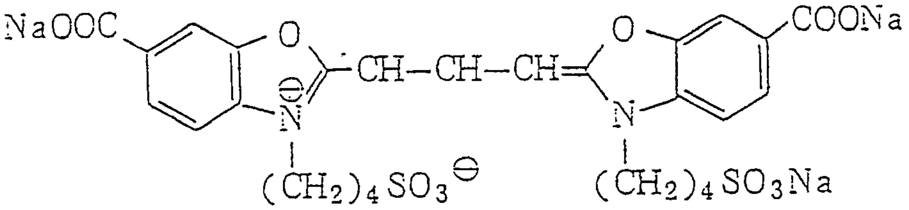

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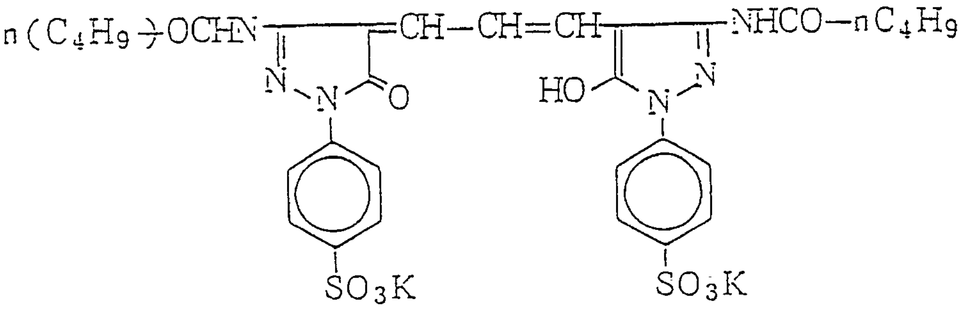

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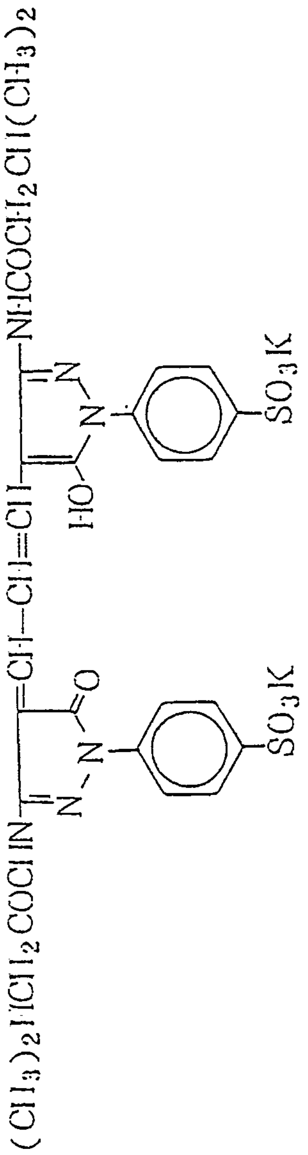

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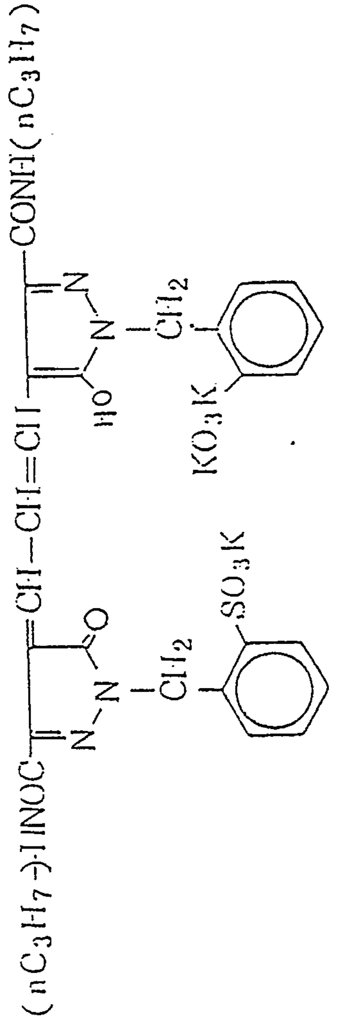
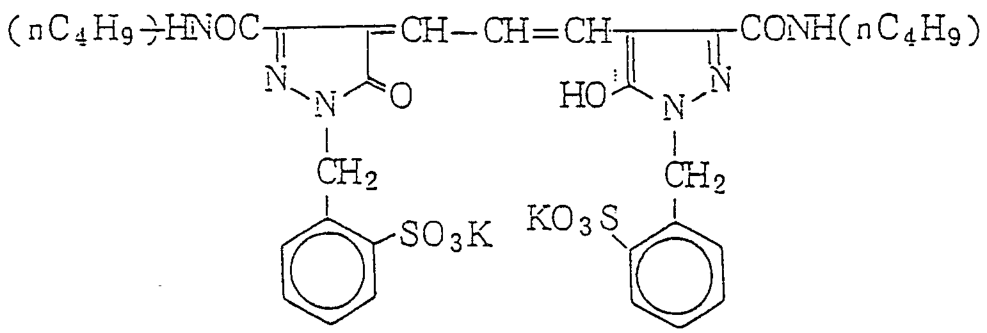


(o)



The mordanting of anionic dyes in a specified layer of the photosensitive material using polymers having cation sites is effective. In this case, the use of a dye which is irreversibly decolorized in the course of the developing, fixing and water washing processes is preferred. The layer containing a dye which has been mordanted using a polymer having cation sites may be an emulsion layer, a surface protective layer or a layer which is on the side of the support opposite from the photographic emulsion layer, but preferably is a layer which is arranged between the emulsion layer and the support. Mordanting of the dye in the underlayer is especially useful for preventing cross-over, for example, in double sided X-ray films for medical purposes.

The methods of solid dispersion disclosed in JP-A-55-155350 and WO88/04794 are also effective as methods for fixing dyes.

The use of a poly(ethylene oxide) based non-ionic surfactant together with a polymer having cation sites is desirable as a coating promotor for the under-layer.

Anion exchange polymers are preferred used as the polymer having cation sites.

Various known quaternary ammonium salt (or phosphonium salt) polymers can be used as the anion exchange polymer. The publications indicated below disclose the use of quaternary ammonium salt (or phosphonium salt) polymers as mordant polymers and anti-static polymers.

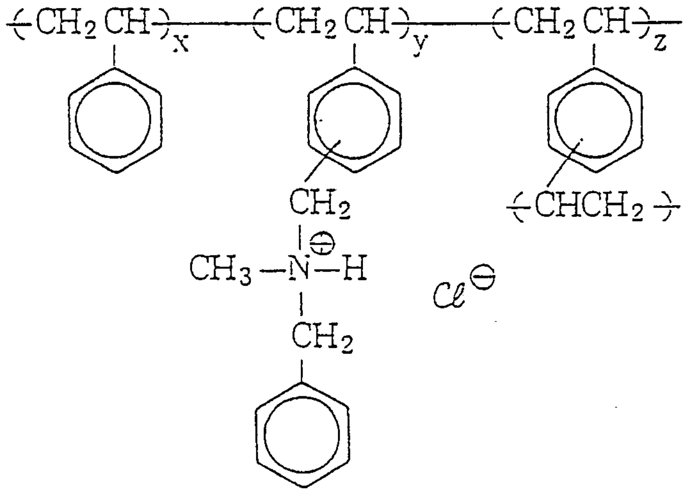
Namely, water dispersed latexes are disclosed in JP-A-59-166940, U.S. Patent 3,958,995, JP-A-55-142339, JP-A-54-126027, JP-A-54-155835, JP-A-53-30328 and JP-A-54-92274, poly(vinyl pyridinium salts) are disclosed in U.S. Patents 2,548,564, 3,148,061 and 3,756,814, water soluble quaternary ammonium salt polymers are disclosed in U.S. Patent 3,709,690, and water insoluble quaternary ammonium salt polymers are disclosed in U.S. Patent 3,898,088.

Moreover, the use of monomers which have at least two (and preferably from two to four) ethylenic unsaturated groups for the preparation of crosslinked water soluble polymer latexes having cation sites is especially desirable for preventing transfer from the mordanting layer to another layer or into the processing baths to thereby prevent photographically undesirable effects.

The polymer mordant is used in an amount of from 5 to 300 mg/m^2, and preferably from 10 to 100 mg/m^2 for one layer containing the polymer mordant.

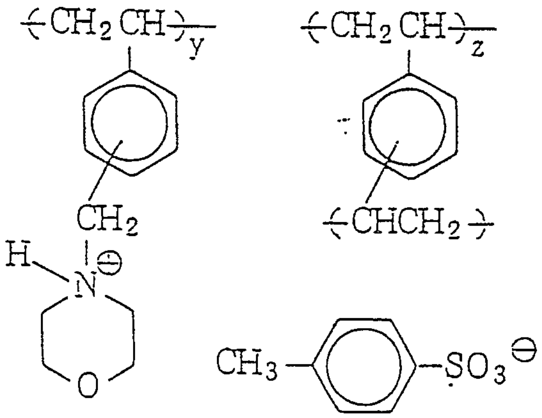
Useful examples of these water-soluble polymer mordant latexes are indicated below.

(A)



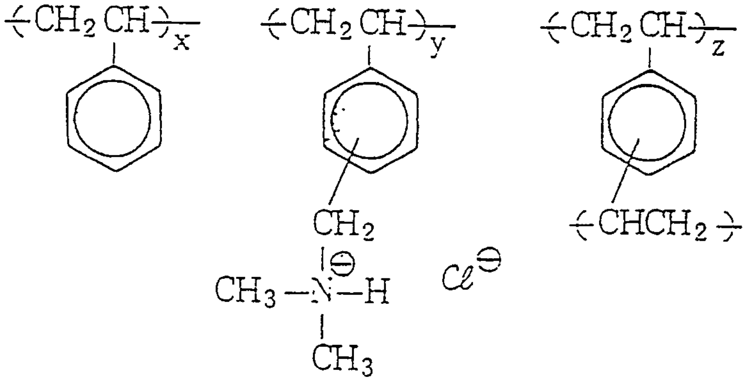
x:y:z=45:45:10 (mol ratio)

(B)



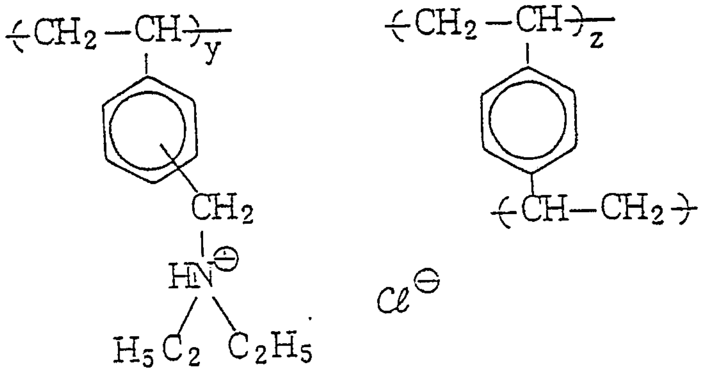
y:z=95:5 (mol ratio)

(C)



x:y:z=45:45:10 (mol ratio)

(D)



y:z=80:20 (mol ratio)

No particular limitation is imposed upon the method used for coating the emulsion layers, surface protective layers, etc. onto the support of the photosensitive material of the present invention but use of the multi-layer simultaneous coating methods disclosed, for example, in U.S. Patents 2,761,418, 3,508,947 and 2,761,791 is desirable.

The developer for use in the present invention can contain the known developing agents. Thus, dihydroxybenzenes (for example, hydroquinone), 3-pyrazolidones (for example, 1-phenyl-3-pyrazolidone) and aminophenols (for example, N-methyl-p-aminophenol) can be used either individually or in combination as the developing agent. The developer generally also contains known preservatives, alkalis, pH buffers and anti-foggants,for example, and may also contain dissolution promotors, color tone controlling agent, development accelerators (for example, quaternary salts, hydrazine, benzyl alcohol), surfactants, anti-foaming agents, hard water softening agents, film hardening agents (for example, glutaraldehyde) and thickeners, for example, as required.

Known and generally used compositions can be used as the fixer. As well as thiosulfate and thiocyanate, the organic sulfur compounds which are known to be effective as fixing agents can be used as the fixing agent for processing the photosensitive material of the present invention. Water soluble aluminum salts may also be included in the fixer as a film hardening agent.

The use of an automatic processor of the roller transport type as disclosed, for example, in U.S. Patents 3,025,779, 3,515,556, 3,573,914 and 3,647,459, and British Patent 1,269,268 is preferred for the method of development processing with an automatic processor in the present invention.

The development temperature is preferably from 18° C to 50° C, in particular from 30° C to 45° C. The development time is preferably from 8 seconds to 40 seconds, in particular from 8 seconds to 25 seconds.

The whole of development processing from the start of development through fixation and water washing to the completion of drying is preferably from 30 seconds to 200 seconds, in particular from 40 seconds to 100 seconds.

No particular limitation are imposed upon the various additives, the method of development and the method of exposure etc. of the photosensitive material of the present invention, and reference can be made to the disclosures of Research Disclosure, Volume 176, Item Number 17643 (December 1978) and ibid, Volume 184, Item Number 18431 (August 1979).

The present invention is described below in greater detail terms with regard to the following non-limiting Examples. All parts are given by weight unless indicated otherwise.

EXAMPLE 1

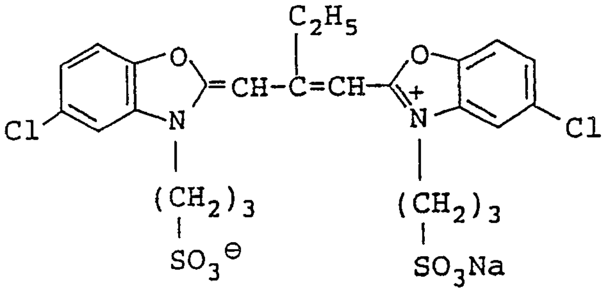
Preparation of Comparative Emulsion A

Potassium bromide (4.5 grams), 20.6 grams of gelatin and 2.5 cc of a 5% aqueous solution of the thioether $HO(CH_2)_2S(CH_2)_2S(CH_2)_2OH$ ware added to 1 liter of water in a reaction vessel. An aqueous solution containing 3.43 grams of silver nitrate, and a second aqueous solution containing 2.97 grams of potassium bromide and 0.363 gram of potassium iodide were added to the reaction vessel over a period of

37 seconds using the double jet method while stirring and maintaining the mixture at a temperature of 65° C. Next, after adding 0.9 gram of potassium bromide, an aqueous solution containing 4.92 grams of silver nitrate was added over a period of 13 minutes. Next, the temperature was raised to 70° C and 18 cc of 25% ammonia solution were added thereto, after which the mixture was neutralized by the addition of 17 cc of 100% acetic acid. An aqueous solution containing 133.49 grams of silver nitrate and an aqueous solution of potassium bromide were then added over a period of 35 minutes using the controlled double jet method such that the potential was maintained at pAg 8.2. The flow rate at this time was increased such that the flow rate at the end of the addition was 2.6 times that at the start of the addition. After the addition had been completed, 15 cc of 2N potassium thiocyanate solution were added and 38.5 cc of a 1% aqueous potassium iodide solution was added over a period of 30 seconds. Subsequently, the temperature was reduced to 35° C and, after removing the soluble salts using a sedimentation method, the temperature was raised to 40° C, 68 grams of gelatin and 2.35 grams of phenoxyethanol were added. The emulsion was then adjusted to pH 6.50 and pAg 8.20 using caustic soda and potassium bromide, respectively.

After raising the temperature to 56° C, 154 mg of 4-hydroxy-6-methyl-1,3-3a,7-tetraazaindene were added and, 10 minutes later, 500 mg of the sensitizing dye (14) having the structure indicated below were added. Moreover, after an additional 10 minutes, 3.3 mg of sodium thiosulfate penta-hydrate, 118 mg of potassium thiocyanate and 2 mg of chloroauric acid were added, and the emulsion was cooled rapidly and solidified after 70 minutes to provide comparative emulsion A.

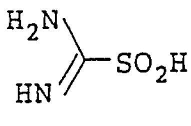
(14)



The emulsion thus obtained was such that 99.5% of the total projected area of all the grains was accounted for by grains having an aspect ratio of at least 3, and the average projected area diameter for all of the grains of aspect ratio 3 or more was 1.35 μm, the standard deviation was 22.3%, the average thickness was 0.200 μm and the average aspect ratio was 6.8.

Preparation of Comparative Emulsion B

Potassium bromide (4.5 grams), 20.6 grams of gelatin and 2.5 cc of a 5% aqueous solution of the thioether $HO(CH_2)_2S(CH_2)_2S(CH_2)_2OH$ were added to 1 liter of water in a reaction vessel. An aqueous solution containing 3.43 grams of silver nitrate and a second aqueous solution containing 2.97. grams of potassium bromide and 0.363 gram of potassium iodide were added to the reaction vessel over a period of 37 seconds using the double jet method while stirring and maintaining the mixture at a temperature of 65° C. Afterwards, 0.1 mg of thiourea dioxide having the structure indicated below was added.



Subsequently, the temperature was raised to 70° C and 18 cc of 25% ammonia solution was added, after which the mixture was neutralized by the addition of 17 cc of 100% acetic acid. An aqueous solution containing 133.49 grams of silver nitrate and another aqueous solution of potassium bromide were then added over a period of 35 minutes using the controlled double jet method such that the potential was maintained at pAg 8.2. The flow rate at this time was increased such that the flow rate at the end of the addition was 2.6 times that at the start of the addition. After the addition had been completed, 15 cc of 2N potassium thiocyanate solution were added and 38.5 cc of a 1% aqueous potassium iodide solution were added over a period of 30 seconds. Subsequently, the temperature was reduced to 35° C. After removing the soluble salts using a sedimentation method, the temperature was raised to 40° C and 68 grams of gelatin and 2.35 grams of phenoxyethanol were added. The emulsion was adjusted to pH 6.50 and pAg 8.20 using caustic soda and potassium bromide, respectively. Thiourea dioxide (0.05 mg) was then added after raising the temperature to 56° C. After stirring the mixture for 20 minutes, 154 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene were added and 10 minutes later, 500 mg of the sensitizing dye (14) were added. Moreover, after an additional 10 minutes, 3.3 mg of sodium thiosulfate penta-hydrate, 118 mg of potassium thiocyanate and 2 mg of chloroauric acid were added, and the emulsion was cooled rapidly and solidified after 70 minutes to provide comparative emulsion B.

The grain size, and aspect ratio, etc. of the emulsion thus obtained were the same, within the limits of error, as those of emulsion A.

Preparation of Emulsions C and D of the Present Invention

Silver halide grains were prepared in the same manner as for emulsion A. After removing the soluble salts using a sedimentation method, the pH and pAg values were adjusted and the temperature was raised to 56° C. Then, 154 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene were added and 5 minutes later, the amount of sodium chloride as indicated in Table 1 was added. Then, after an additional period of 5 minutes, 500 mg of the sensitizing dye (14) were added. The emulsions thus prepared were then chemically sensitized in the same manner as emulsion A to obtain emulsions C and D of the present invention.

Preparation of Emulsions E and F of the Present Invention

Silver halide grains were prepared in the same manner as for emulsion B. After removing the soluble salts using a sedimentation method, the pH and pAg values were adjusted. The temperature was raised to 56° C, and 0.05 mg of thiourea dioxide was added. Then, after stirring for 20 minutes, 154 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindenewere added and 10 minutes later, 500 mg of the sensitizing dye (14) was added. 5 minutes after that, the amount of sodium chloride indicated in Table 1 was added. After an additional period of 5 minutes, the same amounts of sodium thiosulfate penta-hydrate, potassium thiocyanate and chloroauric acid as used in emulsion B were added. Chemical sensitization was then carried out in the same manner as emulsion B to obtain emulsions E and F of the present invention.

Preparation of Emulsion G of the Present Invention

After forming silver halide grains in the same manner as for emulsion B and removing the soluble salts using a sedimentation method, the pH and pAg were adjusted. Then, the amount of sodium chloride as indicated in Table 1 was immediately added, after which the emulsion was chemically sensitized in the same manner as emulsion B to provide emulsion G of the present invention.

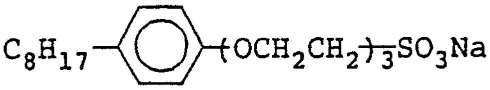
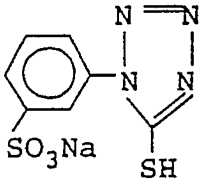
Preparation of Comparative Emulsion H

While preparing emulsion B, the amount of sodium chloride indicated in Table 1 was added all at once 17 minutes after starting the addition using the controlled double jet method and maintaining a pAg value of 8.2, after which the controlled double jet addition was continued for an additional 18 minutes. An emulsion similar to that of emulsion B was prepared, namely, an emulsion prepared by adding NaCl during grain formation to obtain comparative emulsion H.

The adsorbed amount of sensitizing dye contained in Emulsions A to H was found to be almost saturated adsorption amount (100%) by a measurement of absorbance of supernatant solution obtained by centrifugation.

Preparation of Emulsion Coating Liquids

The reagents indicated below were added per mol of silver halide to emulsions A to H, to obtain emulsion, coating liquids.

Polymer Latex (Poly(ethyl acrylate/methacrylic acid)=97/3)	20.0 g
Film Hardening Agent 1,2-Bis(vinylsulfonylacetamido)ethane	2.4 g
2,6-Bis(hydroxyamino)-4-diethylamino-1,3,5-triazine	76 mg
Poly(sodium acrylate) (Average molecular weight 41,000)	2.1 g
Poly(sodium styrenesulfonate) (Average molecular weight 600,000)	1.0 g
Dextran (Average molecular weight 39,000)	23.6 g
Trimethylolpropane	9.8 g
Hydroquinone mono-sulfonic acid Potassium salt	9.7 g
	0.6 g
	32 mg

Preparation of the Support

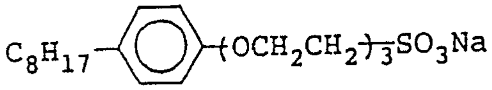
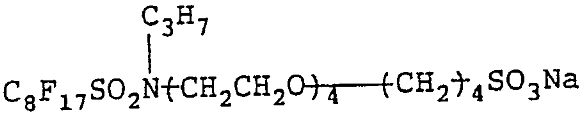
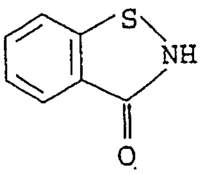
A base was prepared by providing an under-layer with a coated weight of gelatin of 84 mg/m^2 on both sides of a blue colored poly(ethylene terephthalate) having a thickness 175 μm.

Preparation of Photographic Materials

The above described coating liquids were coated onto both sides of the above described base simultaneously with a surface protective layer coating liquid.

The coated silver weight was 1.95 g/m^2 per side, and the base was coated on both sides thereof.

The surface protective layer was prepared such that the coated weight of each component was as indicated below, to obtain the photographic materials 1 to 8 as shown in Table 1.

Contents of the Surface Protective Layer	Coated Weight (per side)
Gelatin	1.138 g/m^2
Dextran (Average molecular weight 39,000)	0.228 g/m^2
4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	0.0155 g/m^2
Poly(sodium acrylate) (Average molecular weight 41,000)	0.023 g/m^2
	0.0225 g/m^2
$C_{16}H_{33}O-(CH_2CH_2O)_{10}-H$	0.035 g/m^2
 $C_8F_{17}SO_2\overset{C_3H_7}{\overset{\vert}{N}}(CH_2CH_2O)_4(CH_2)_4SO_3Na$	0.0005 g/m^2
$C_8F_{17}SO_3K$	0.0053 g/m^2
Poly(methyl methacrylate) (Average particle size 3.7 µm)	0.088 g/m^2
Proxell (produced by Imperial Chemical Industry, Co. and having the following formula) 	0.0006 g/m^2

Evaluation of Photographic Performance

The photographic materials 1 to 8 were subjected to a 1/10th second exposure on both sides thereof using green light having a peak at 550 nm, after which the photographic materials were subjected to SP processing (dry to dry time 45 seconds) in an FPM9000 automatic processor made by the Fuji Photo Film Co. Ltd. using developer RD7 and fixer Fuji F made by the same company.

The photographic speed was evaluated as the reciprocal of the exposure which gave a density of fog +1.0, and the values are shown in Table 1 as relative values taking the speed for photographic material 1 to be 100.

Fog represents the total value including the support density. The fog value on processing the support itself in the above described automatic processor was 0.125.

Evaluation of Pressure Sensitivity

Photographic materials (35 mm x 120 mm) 1 to 8 were stored for 1 hour under conditions of 25°C, 25%, RH and then a stainless steel pipe of diameter 6 mm was set on the center of longitudinal direction of the photographic material (35 x 120 mm) and folded through 180° under the same conditions. The folding speed was such that the sample was folded through 180° in 1 second and then returned to the original state within the next 1 second. The thus handled photographic materials were exposed and processed as described above in order to evaluate the photographic performance 30 minutes after the materials were folded.

At this time, the increase in density of the portion of the photographic material which had blackened in the form of a band corresponding to the stainless steel pipe (excluding the fog density of the emulsion and the base density) was measured using a Macbeth densitometer. The results obtained are shown in Table 1.

From the results shown in Table 1, it is clearly seen that the present invention provides improved balance between photographic speed and pressure sensitivity. Moreover, photographic materials 5 to 7 of the present invention in which reduction sensitization had been carried out were especially good when compared with the comparative materials in terms of photographic speed and pressure sensitivity. Furthermore, in comparison to comparative material 8 to which sodium chloride was added during grain formation, the samples of the invention in which the sodium chloride was added had been after grain formation clearly provided improved pressure resistance.

Table 1

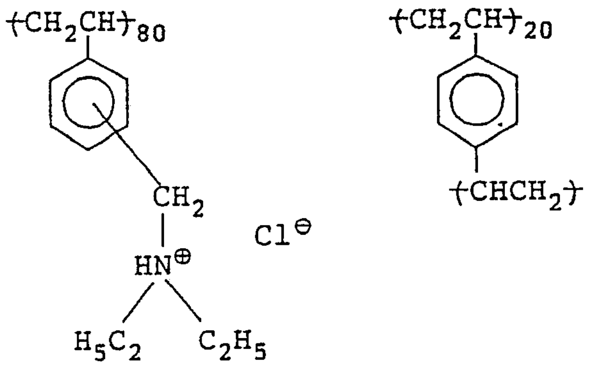
Photographic Material	Emulsion Used	Addition Amount of Sodium Chloride (g/mol·Ag)	Photographic Speed	Fog	Increase in Density due to Pressure ΔD
1 (Comp. Ex.)	A	None	100	0.150	0.102
2 (")	B	None	126	0.155	0.126
3 (Invention)	C	1.44	100	0.150	0.080
4 (")	D	2.88	100	0.150	0.060
5 (")	E	1.44	126	0.152	0.098
6 (")	F	2.88	126	0.152	0.072
7 (")	G	2.88	126	0.152	0.072
8 (Comp. Ex.)	H	2.88	126	0.155	0.113

Photographic Material	Time of Addition of Sodium Chloride
1 (Comp. Ex.)	None
2 (")	
3 (Invention)	Added immediately after de-salting and forming tabular grains, but prior to chemical sensitization
4 (")	"
5 (")	Added during chemical sensitization
6 (")	"
7 (")	Added immediately after de-salting, but prior to chemical sensitization
8 (Comp. Ex.)	Added during grain formation

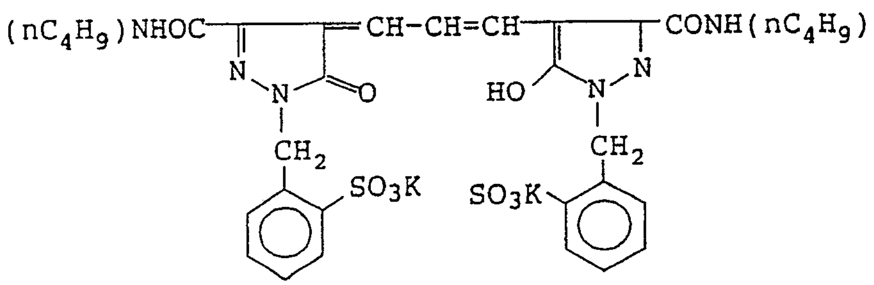
EXAMPLE 2

Photographic materials were prepared in the same manner as in Example 1, except that an under-layer with the coated weights indicated below was provided on each side of the support used in Example 1.

Gelatin 84 mg/m^2



60 mg/m^2



17 mg/m^2

The process described below was used when evaluating the photographic performance and pressure sensitivity of the thus prepared photographic materials.

The results obtained were the same as those described in Example 1, and there was no change even though the preparation of the support and the method of processing were different. The present invention is therefore broadly applicable to a variety of photographic materials and processing conditions.

Development Process

Preparation of Concentrates

Developer

Part A

Potassium hydroxide	330 g
Potassium sulfite	630 g
Sodium sulfite	240 g
Potassium carbonate	90 g
Boric acid	45 g
Diethylene glycol	180 g
Diethylenetriamine pentaacetic acid	30 g
3,3'-Dithiobishydrocinnamic acid	3 g
5-Methylbenzotriazole	0.025 g
Hydroquinone	450 g
Potassium bromide	15 g
Water to make	4125 ml

Part B

Triethylene glycol	525 g
Glacial acetic acid	102.6 g

5-Nitroindazole	3.75 g
1-Phenyl-3-pyrazolidone	34.5 g
Water to make	750 ml

Part C

Glutaraldehyde (50 wt/wt%)	150 g or 0
Potassium metabisulfite	150 g
Water to make	750 ml

Fixer (Single Reagent)

Ammonium thiosulfate (70 wt/vol%)	200 ml
Ethylenediamine tetraacetic acid, disodium salt, dihydrate	0.03 g
Sodium thiosulfate pentahydrate	10 g
Sodium sulfite	15 g
Boric acid	4 g
1-(N,N-dimethylamino)ethyl-5-mercaptotetrazole	1 g
Tartaric acid	3.2 g
Glacial acetic acid	31.5 g
Sodium hydroxide	11 g
Sulfuric acid (36N)	3.9 g
Ammonium sulfate	10 g
Water to make	400 ml
pH	4.65

Preparation of the Developer

Each part of the developer concentrate described above was placed into a polyethylene container. These containers were combined such that the containers for parts A, B and C formed a single unit.

Furthermore, the fixer concentrate described above was also placed into a polyethylene container.

The developer and fixer were charged into the development tank and the fixer tank of the automatic processor, respectively, in the proportions indicated below using quantitative delivery pumps provided in the processor.

Developer

Part A	55 ml
Part B	10 ml
Part C	10 ml
Water	125 ml
pH	10.50

Fixer

Concentrate	80 ml
water	120 ml
pH	4.65

The water washing tank was filled with municipal water. Four bags of non-woven cloth enclosing 50 grams each of a slow silver releasing agent (trade name "Biosure SG" made by the Kinki Pipe Technology (Co.)) containing 0.5 wt% of Ag_2O in a soluble glass comprising $Na_2O/B_2O_5/SiO_2$ were submerged in the bottom of the tank.

Automatic Processor Construction

The construction of the automatic processor used is outlined below.

	Tank Liquid Volume	Processing Temperature	Processing Path Length	Processing Time[1]
Development	15 ℓ	35°C	613 mm	13.3 sec.
(Liquid Surface Area/Tank Capacity = 35 cm^2/liter)				
Fixation	15 ℓ	32°C	541 mm	11.7 sec.
Water Wash	13 ℓ	17°C Running Water	305 mm	5.7 sec.
Squeeze				6.6 sec.
Drying		58°C	368 mm	8.0 sec.
Total			1827 mm	45.3 sec.

Processing

The above described photosensitive materials were subjected to an X-ray exposure and developed and processed using the developer which had been mixed in the proportions indicated above in the above described automatic processor, with replenishment at the rate of 25 ml of developer and 25 ml of fixer per quarter plate size sheet (10×12 inches).

The wash water flow rate was 10 liters per minute. As the photosensitive material was being processed, an electromagnetic valve opened and wash water was supplied thereto (about 1 liter per quarter plate size sheet). At the end of operation each day, an electromagnetic valve was opened automatically and all the water was removed from the tank.

Processing runs were carried out in this way until the developer and fixer had each reached a running equilibrium composition, and the photographic performance of the photographic materials was evaluated after reaching the running equilibrium compositions.

EXAMPLE 3

Potassium bromide (5 grams), 0.05 gram of potassium iodide, 30 grams of gelatin and 2.5 cc of a 5% aqueous solution of the thioether $HO(CH_2)_2S(CH_2)_2S(CH_2)_2OH$ were added to 1 liter of water in a reaction vessel. An aqueous solution containing 6.49 grams of silver nitrate and a second aqueous solution containing 5.72 grams of potassium bromide and 0.70 gram of potassium iodide were added to the reaction vessel over a period of 45 seconds using the double jet method while stirring and maintaining the mixture at a temperature of 75° C. Next, after adding 2.92 grams of potassium bromide, an aqueous solution containing 10.19 grams of silver nitrate was added over a period of 13 minutes. Then, an aqueous solution containing 166.90 grams of silver nitrate and an aqueous solution of potassium bromide were added over a period of 30 minutes using the controlled double jet method in such that the potential was maintained at a pAg value of 8.1. The flow rate at this time was such that the flow rate at the end of the addition was 6.8 times that at the start of the addition. After the addition had been completed, 15 cc of 2N potassium thiocyanate solution were added and then 61 cc of a 1% aqueous potassium iodide solution were added over a period of 30 seconds. Subsequently, the temperature was reduced to 35° C. After removing the soluble salts using a sedimentation method, the temperature was raised to 40° C, and 95.4 grams of gelatin and 2.5 grams of phenol were added. The emulsion was adjusted to pH 6.50 and pAg 8.20 using caustic soda and potassium bromide, respectively. The temperature was then raised to 56° C and 174 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was added, and 10 minutes later, 668 mg of the sensitizing dye (14) were added. After an additional period of 10 minutes, 4.7 mg of sodium thiosulfate penta-hydrate, 157 mg of potassium thiocyanate and 4.5 mg of chloroauric acid were added to the emulsion and the mixture was cooled rapidly and solidified after 70 minutes to provide emulsion I.

The emulsion obtained was much that 93% of the total projected area of all the grains was accounted for by grains of which the aspect ratio was at least 3, and of all the grains having an aspect ratio at least 2, the average projected area diameter was 0.93 μm, the standard deviation was 43.8%, the average thickness was 0.182 μm and the aspect ratio was 6.9. Furthermore, the amount of sensitizing dye was 102% of the amount adsorbed at saturation.

Preparation of Emulsion Coating Liquids

The reagents indicated below were added per mol of silver halide to emulsion I to obtain coating liquids.

Polymer latex (Poly(ethyl acrylate/methacrylic acid) = 97/3)	24.2 g
Film hardening agent 1,2-Bis(vinylsulfonylacetamido)ethane	3.5 g
2,6-Bis(hydroxyamino)-4-diethylamino-1,3,5-triazine	92 mg
Poly(sodium acrylate) (Average molecular weight 400,000)	2.6 g
Poly(sodium styrenesulfonate) (Average molecular weight 600,000)	0.78 g
Polyacrylamide (Average molecular weight 41,000)	28.8 g
Potassium bromide	75 mg
Sodium chloride or potassium chloride	Amount shown in Table 2

Preparation of the Support

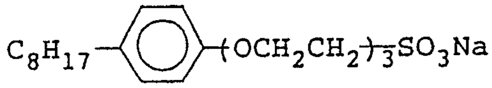
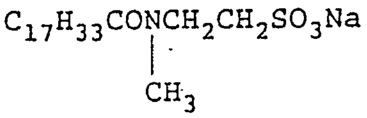
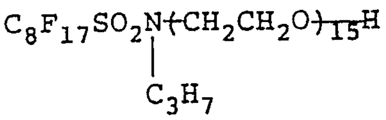
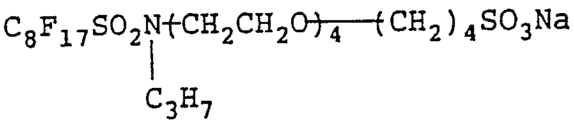
The support was prepared in the same manner as in Example 2.

Preparation of Photographic Materials

The above described coating liquids were simultaneously coated onto both sides of the above described support together with a surface protective layer coating liquid as described below.

The coated silver weight was 1.63 g/m^2 per side and the base was coated on both sides thereof.

The surface protective layer was prepared in such that the coated weight of each component, per side, was as indicated below, to obtain the photographic materials 9 to 13 shown in Table 2.

Contents of the Surface Protective Layer	Coated Weight
Gelatin	0.966 g/m^2
Polyacrylamide (Average molecular weight 45,000)	0.227 g/m^2
4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	0.0155 g/m^2
Poly(sodium acrylate) (Average molecular weight 400,000)	0.023 g/m^2
	0.013 g/m^2
$C_{16}H_{33}O(CH_2CH_2O)_{10}H$	0.045 g/m^2
 $C_{17}H_{33}CO\underset{\underset{CH_3}{\vert}}{N}CH_2CH_2SO_3Na$	0.065 g/m^2
 $C_8F_{17}SO_2\underset{\underset{C_3H_7}{\vert}}{N}(CH_2CH_2O)_{15}H$	0.003 g/m^2
 $C_8F_{17}SO_2\underset{\underset{C_3H_7}{\vert}}{N}(CH_2CH_2O)_4(CH_2)_4SO_3Na$	0.001 g/m^2
Poly(methyl methacrylate) (Average particle size 3.7 μm)	0.087 g/m^2
Chlorohydroquinone	0.046 g/m^2
Proxell	0.0005 g/m^2

The thus prepared photographic materials were folded, exposed and processed as in Example 1. Photographic performance and pressure sensitivity were evaluated in the same manner as in Example 1.

The results obtained are shown in Table 2.

It is clearly seen from Table 2 that the present invention provides enhanced balance between photographic speed, fogging and pressure resistance as compared to comparative material 9.

Table 2

Photographic Material	Chlorine Containing Inorganic Compound	2)Addition Amount of Chlorine Containing Compound (mmol/mol·Ag)	1)Photographic Speed	Fog	Increase in Density due to Pressure ΔD
9 (Comp. Ex.)	None	-	100	0.150	0.080
10 (Invention	Sodium Chloride	29.5	100	0.150	0.062
11 (")	"	58.9	98	1.149	0.050
12 (")	Potassium Chloride	29.5	100	0.150	0.061
13 (")	"	58.9	98	0.149	0.050

1) The photographic speeds are shown as relative speeds taking the speed for photographic material 9 to be 100.

2) Chlorine containing inorganic compound added after chemical sensitization, but prior to coating.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A silver halide photographic photosensitive material comprising a support having thereon at least one hydrophilic colloid layer, at least one layer of which is a photosensitive silver halide emulsion layer comprising tabular silver halide grains having an aspect ratio of at least 3, said photosensitive silver halide emulsion layer being prepared by reacting a water soluble silver salt with a water soluble alkali halide to form an emulsion comprising tabular silver halide grains, de-salting the thus formed emulsion, chemically sensitizing the emulsion and coating the resulting chemically sensitized emulsion comprising tabular silver halide grains onto the support, wherein a chloride of an element or ion selected from the group consisting of Na, K, Mg, Ca, Li and NH_4^+ is added to said emulsion either immediately after de-salting, after de-salting but prior to chemical sensitization, during chemical sensitization, after chemical sensitization but prior to coating, or immediately prior to coating.

2. A silver halide photographic photosensitive material as in claim 1, wherein the silver halide grains constituting said photosensitive silver halide emulsion layer are subjected to reduction sensitization.

3. A silver halide photographic photosensitive material as in claim 1, wherein said tabular silver halide grains are spectrally sensitized with a sensitizing dye in an amount of at least 80% of the amount for saturated adsorption of the silver halide grains.

4. A silver halide photographic photosensitive material as in claim 1, wherein said chloride is selected from sodium chloride, potassium chloride, calcium chloride, magnesium chloride lithium chloride and ammonium chloride.

5. A silver halide photographic photosensitive material as in claim 1, wherein said chloride is added to said emulsion comprising tabular silver halide grains after de-salting but prior to chemical sensitization, after chemical sensitization but prior to coating, or immediately before coating.

6. A silver halide photographic photosensitive material as in claim 1, wherein said chloride is added to the emulsion comprising tabular silver halide grains after de-salting but prior to chemical sensitization.

7. A silver halide photographic photosensitive material as in claim 1, wherein said chloride is added in an amount of from 5 to 200 mmol per mol of silver contained in the emulsion comprising tabular silver halide grains.

8. A silver halide photographic photosensitive material as in claim 2, wherein said reduction sensitization is carried out during growth of the silver halide grains.

9. A silver halide photographic photosensitive material as in claim 1, wherein said tabular silver halide grains are spectrally sensitized with a sensitizing dye in an amount of at least 100% but not more than 200% of the amount for saturated adsorption of the silver halide grains.

10. A silver halide photographic photosensitive material as in claim 1, wherein at least 50% of the total projected area of the silver halide grains constituting the photosensitive silver halide emulsion layer is accounted for by tabular silver halide grains having an aspect ratio of at least 3.

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 0458

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)
Y,D	PATENT ABSTRACTS OF JAPAN vol. 13, no. 291 (P-893)(3639), 6 July 1989; & JP - A - 0172141 (FUJI) 17.03.1989 – – –	1-10	G 03 C 1/035 G 03 C 1/08 G 03 C 1/34 // G 03 C 5/16
Y	DATABASE WPIL/DERWENT accession no. 88-209397 (30), 1988, Derwent Publications Ltd., London, GB; & JP - A - 63146032 (KONISHIROKU) 18.06.1988 – – –	1-10	
A	EP-A-0 138 543 (FUJI) * claims 1,5,32 * – – –	1,7	
A	EP-A-0 285 308 (3M) * claims; page 11, lines 6-15 * – – –	1-10	
A	EP-A-0 348 934 (FUJI) * claims; page 14, lines 24-48 * – – – – –	1,2,10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G 03 C 1/00 G 03 C 5/00

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
Berlin	26 April 91	STOCK H

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
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
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