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(54) **Light-sensitive silver halide photographic material feasible for high speed processing.**

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GB-A- 2 096 782
US-A- 3 369 902
US-A- 3 425 857
US-A- 4 172 730
US-A- 4 551 424
US-A- 4 555 480

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Description

This invention relates to a light-sensitive silver halide photographic material suitable for high speed processing. It particularly relates to a light-sensitive silver halide photographic material having high sensitivity and excellent pressure resistance and graininess even when subjected to ultra rapid processing.

In recent years, light-sensitive silver halide photographic materials have been consumed in ever increasing quantities. For this reason, there has also been an increase in the number of sheets required for the processing of light-sensitive silver halide photographic materials, and it has been desired to carry out the processing more rapidly, in other words to increase the quantity processed in a given time.

The above trend is also seen in the field of X-ray light-sensitive materials, for example X-ray films for medical use. More specifically, with a rapid increase in the frequency of diagnosis caused by the encouragement of periodical health examinations, more accurate diagnosis is desired which increases the items to be checked and increases the number of sheets used in the X-ray photography.

On the other hand, it is also necessary to obtain the diagnosis result as soon as possible.

Thus there are strong demands for carrying out the processing more rapidly than ever to facilitate diagnosis. In particular, in, for example, angiography or perioperative photography, it is necessary to look at photographs in as short a time as possible.

In order to satisfy the above demands in the medical field, it is necessary to promote automatization (e.g. of photography or conveyance) of the diagnosis, and also to process the X-ray films more rapidly.

However, ultra rapid processing causes problems such that, for example, (a) the density is insufficient (i.e. there is a decrease in sensitivity, contrast and maximum density), (b) the fixing cannot be carried out sufficiently, (c) the water washing of films may be insufficient, and (d) the drying of films may be insufficient. Insufficient fixing and insufficient water washing may cause a change in the tone of films during storage thereof and consequently lower image quality.

A means to solve these problems is to decrease the amount of gelatin. However, a decrease in the amount of gelatin tends to bring about problems such as coating uneveness and coating streaks. Also when films with less gelatin rub each other or are rubbed by other materials, so-called abrasion blackening may occur after processing to form a portion having a higher density than other portions.

Ultra rapid processing is desired as mentioned above. In the present specification, ultra rapid processing is a processing for a total of 20 to 60 seconds from the time during which the top end of a film is first inserted into an automatic processor, passed through a developing tank, a gangway, a fixing tank, a gangway, a washing tank, a gangway and a drying spot, and emitted from the drying spot [in other words, the quotient (s) obtained by dividing the total length (m) of a processing line by the line conveyor speed (m/s)]. The reason why the time for the gangways is included is, as well known in the present industrial field, a processing solution used in a preceding step may also swell at a gangway and the processing step is considered to substantially proceed in the gangway.

To promote rapid processing, it is very important to control the surface tension and viscosity of the coating solutions used for forming an outermost layer and a layer adjacent thereto which constitute a light-sensitive silver halide photographic material. In particular, a bead coating technique for improving the viscosity of a coating solution is disclosed in Japanese Unexamined Patent Publications No. 115214/1977, No. 1350/1979 and No. 108566/1981. Many attempts have been made to provide better photographic layers. For example, in the lowermost layer in a light-sensitive material, the amount of coating solution and the viscosity are from 2 to 12 g/m^2 and 1 to 8 cp, respectively (Japanese Unexamined Patent Publication No. 115214/1977), or the relationship between the viscosity η_0 of a coating solution for a lowermost layer and the viscosity η_1 of a coating solution for a layer directly above the lowermost layer is such that $\eta_0 = \eta_1 \pm 10$ (cp) when the lowermost layer is coated at a low shear rate, and $\eta_0 < \eta_1$ when the lowermost layer is coated at a high shear rate (Japanese Unexamined Patent Publication No. 108566/1981).

Japanese Patent Publication No. 47045/1976 discloses the importance of the amount of gelatin in rapid processing, in which, however, the total processing time is 60 to 120 seconds including the time for gangways. Such a processing time, however, cannot satisfy the demands for ultra rapid processing as recently practiced.

Furthermore, in recent years, with an increase in medical X-ray examinations in particular, there is a strong demand to decrease exposure doses in the field of medical science due to international public opinion. To meet such a demand, there have been used fluorescent intensifying paper, intensifying screens, fluorescent screens and X-ray image amplifiers. A remarkable improvement is seen in these and an increase in the sensitivity of X-ray light-sensitive photographic materials. On the other hand, to carry out examinations more precisely, there is a demand for high precision X-ray photography. Since the precision proportionally increases with greater X-ray irradiation, an X-ray photographing technique utilizing a larger

radiation dose has been developed, and a large volume X-ray generator has been developed. However, the photographing techniques requiring such a large radiation dose rather contradict the above demands for decreasing exposure doses, and cannot be said to be preferable. Accordingly, in the field of X-ray photography less exposure and yet higher precision is desired. Thus, a photographic material that can provide a precise image, in other words, a photographic material having higher sensitivity with a reduced X-ray dose is sought.

Many and various techniques are available to increase sensitivity, i.e. sensitizing methods, with the same grain size. Thus it is expected that the sensitivity can be increased while keeping the same grain size, namely while maintaining the covering power, if an appropriate sensitizing technique is used. Many reports have been made on such techniques, including, for example, a method in which a development accelerator such as a thioether is added to an emulsion, a method in which a spectrally sensitized silver halide emulsion is subjected to hypersensitization by the use of a suitable combination of dyes, or a method using optical sensitizers. These methods, however, do not necessarily have suitable properties when used in high sensitivity light-sensitive silver halide photographic materials. In other words, the high sensitivity light-sensitive silver halide photographic materials, which are chemically sensitized to the maximum possible extent, tend to be fogged during storage when the above methods are applied.

Moreover, in the field of medical X-ray photography orthochromatic light-sensitive materials, which are made light-sensitive in the wavelength region of 540 to 550 nm by carrying out orthochromatic sensitization, rather than regular materials conventionally having a light-sensitive region at 450 nm, have been used. These materials have a wide light-sensitive wavelength region and a higher sensitivity. Accordingly, they can decrease the exposure of X-ray doses and minimize their influence on human bodies. Thus, dye sensitization is a very useful sensitizing means, but it still has unsolved problems. For example, there remains a problem that sufficient sensitivity cannot be obtained depending on the photographic emulsions used.

Pressure desensitization (i.e., desensitization at the time of development by mechanical pressure applied before exposure) may sometimes occur due to mechanical pressure applied before exposure. For instance, in medical X-ray films, which have a large size, film folding such as the so-called knick mark folding may sometimes occur when a film is folded by its own weight at a portion where the film is held causing pressure desensitization. Also, nowadays, an automatic exposing and developing apparatus utilizing a mechanical conveyance is widely used in medical X-ray photographic systems. In such an apparatus, however, mechanical force may be applied to films, whereby the above-mentioned pressure blackening and pressure desensitization tend to occur, especially in a dry place in winter. Such a phenomenon is likely to cause serious difficulties in medial diagnosis. In particular, it is well known that light-sensitive silver halide photographic materials comprising silver halide grains having a large grain size and high sensitivity are more likely to have pressure desensitization.

As materials aiming to improve the response to pressure desensitization, those using thallium or those using a dye are disclosed in U.S. Patents No. 2,628,167, No. 2,759,822, No. 3,455,235 and No. 2,296,204, French Patent No. 2,296,204 and Japanese Unexamined Patent Publications No. 107129/1976 and No. 116025/1975, but the improvement is insufficient or dye stains may occur to a great extent. Other materials cannot necessarily be said to have sufficiently provided a light-sensitive silver halide photographic material having high sensitivity, comprising large grain size silver halide emulsions and chiefly utilizing ordinary surface sensitivity.

On the other hand, various attempts have been made to decrease the pressure desensitization by changing the binder properties of light-sensitive silver halide photographic materials, as disclosed, for example, in U.S. Patents No. 3,536,491, No. 3,775,128, No. 3,003,878, No. 2,759,821 and No. 3,772,032, and in Japanese Unexamined Patent Publications No. 3325/1978, No. 56227/1975, No. 147324/1975 and No. 141625/1976. However, although an improvement has been made in respect of pressure sensitization by these techniques, no fundamental improvement has been achieved as there may seriously occur the sticking of film surfaces or the deterioration of binder properties such as dryness and scratching.

The present invention seeks to provide a light-sensitive silver halide photographic material that can eliminate the above problems even when high speed processing is carried out, for example, even when ultra rapid processing whose total processing time is 20 to 60 seconds as mentioned above is carried out, and which has excellent sensitivity, contrast, maximum density, fixing performance and dryness.

The present invention also seeks to provide a light-sensitive silver halide photographic material that has been produced with less problems in coating even with a reduced amount of gelatin, that suffers less abrasion blackening or pressure desensitization, and that has excellent in graininess.

The present invention provides a light-sensitive silver halide photographic material which comprises photographic layers which have been applied under conditions such that the surface tension of a coating

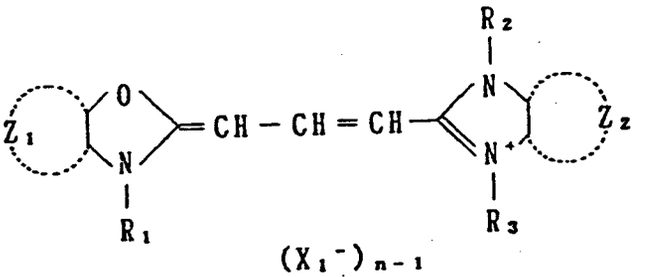
solution for forming an outermost layer is $6x10^{-3}$ N/m (6 dyn/cm) or more less than the surface tension of a solution for forming the layer adjacent to the outermost layer, which photographic material satisfies at least one of the conditions:

(a) the amount of gelatin contained in all of the layers on at least the side of the support having a light-sensitive silver halide emulsion layer and a hydrophilic colloid layer is from 2.20 to 3.10 g/m^2,

(b) the coating solution for forming the outermost layer and the solution for forming the layer adjacent thereto each have a viscosity of $20x10^{-3}$ Pas (20 cp) or less.

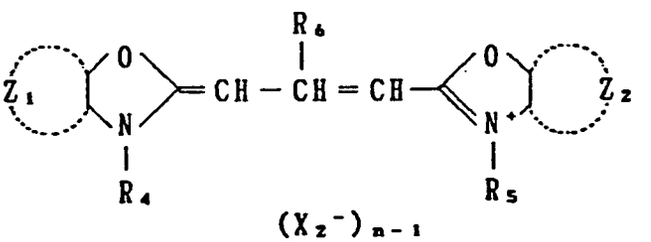
According to a preferred embodiment of this invention, the photographic material comprises at least one silver halide emulsion layer containing at least one compound of formulae (I), (II) and (III):

Formula (I):



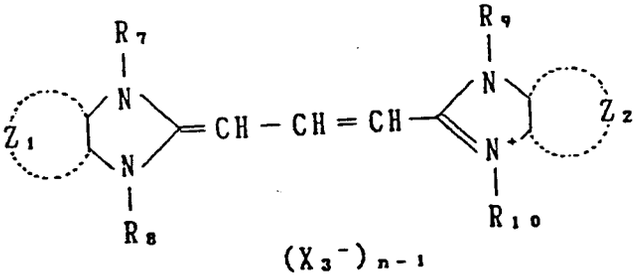
wherein R_1, R_2 and R_3, which may be identical or different, each represents a substituted or unsubstituted alkyl group, alkenyl group or aryl group, at least one of R_1 and R_3 representing a sulfoalkyl group or a carboxyalkyl group; X_1^- represents an anion; Z_1 and Z_2, which may be identical or different, each represents a group of nonmetallic atoms which together with the carbon atoms to which it is attached forms a substituted or unsubstituted carbon ring; and n is 1 or 2, with the proviso that n is 1 when an intramolecular salt is formed;

Formula (II):



wherein R_4 and R_5, which may be identical or different, each represents a substituted or unsubstituted alkyl group, alkenyl group or aryl group, at least one of R_4 and R_5 representing a sulfoalkyl group or a carboxyalkyl group; R_6 represents a hydrogen atom, a lower alkyl group or an aryl group; X_2^- represents an anion, Z_1 and Z_2, which may be identical or different, each represents a group of nonmetallic atoms which, together with the carbon atoms to which it is attached, forms a substituted or unsubstituted carbon ring; and n is 1 or 2, with the proviso that n is 1 when an intramolecular salt is formed;

Formula (III):



wherein R_7 and R_9, which may be identical or different, each represents a substituted or unsubstituted lower alkyl group; R_8 and R_{10}, which may be identical or different, each represents a lower alkyl group, a hydroxyalkyl group, a sulfoalkyl group or a carboxyalkyl group; X_3^- represents an anion, Z_1 and Z_2, which may be identical or different, each represent a group of nonmetallic atoms which, together with the carbon atoms to which it is attached, forms a substituted or unsubstituted carbon ring; and n is 1 or 2, with the proviso that n is 1 when an intramolecular salt is formed.

In this invention, the photographic layers have been applied under conditions such that the surface tension of a solution for forming an outermost layer (usually the uppermost layer) is $6x10^{-3}$ N/m (6 dyn/cm) or more less than the surface tension of a solution for forming the layer adjacent to the outermost layer (usually the layer directly under the uppermost layer). In order to make the difference $6x10^{-3}$ N/m (6 dyn/cm) or more one embodiment is to use at least one surface active agent in the outermost layer. The surface active agent may or may not be used in the layer directly under the outermost layer. The surface active agents used in the outermost layer and the layer directly under it may be the same or different.

The difference in the surface tension between the solutions used for the outermost layer and the layer directly under it is preferably not less than $8x10^{-3}$ N/m (8 dyn/cm), more preferably not less than $10x10^{-3}$ N/m (10 dyn/cm), and most preferably not less than $12x10^{-3}$ N/m (12 dyn/cm).

Usually, the "outermost layer" mentioned in this invention refers literally to the outside layer, and, in general, is the uppermost layer as mentioned above. A coating, for example a super coat, formed by spraying or coating is sometimes provided on the outermost layer.

The surface active agent usable in this invention includes, for example, nonionic surface active agents such as saponin (steroid type), alkylene oxide derivatives (for example, polyethylene glycol, a polyethylene glycol/polypropylene glycol condensate, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or amides, and addition products of silicones with polyethylene oxides), glycidol derivatives (for example, alkenylsuccinic acid polyglycerides, and alkylphenol polyglycerides), aliphatic acid esters of polyhydric alcohol and alkyl esters of sugar. It also includes anionic surface active agents containing an acidic group such as a carboxyl group, a sulfo group, a phospho group, a sulfuric acid ester group and a phosphoric acid ester group, including alkyl carboxylates, alkyl sulfonates, alkyl benzenesulfonates, alkyl naphthalenesulfonates, alkylsulfuric acid esters, alkylphosphoric acid esters, N-acyl-N-alkyltaurines, sulfosuccinic acid esters, sulfoalkyl polyoxyethylene alkylphenyl ethers and polyoxyethylene alkylphosphoric acid esters. It further includes amphoteric surface active agents such as amino acids, aminoalkylsulfonic acids, aminoalkylsulfuric acid or phosphoric acid esters, alkylbetaines and amine oxides. It also includes cationic surface active agents such as alkylamine salts, aliphatic or aromatic quaternary ammonium salts, heterocyclic quaternary ammonium salts such as pyridinium and imidazolium, phosphonium or sulfonium salts containing an aliphatic or a heterocyclic ring. There may be further used, for example, fluorine-containing surface active agents or fluorine-containing surface active agents having a polyoxyethylene group.

The surface active agents of alkylene oxide type are disclosed in, for example, Japanese Patent publication No. 9610/1976, DT-26 48 746 and Japanese Unexamined Patent Publications No.129623/1978, No. 89624/1979, No. 98235/1979, 203435/1983, No. 208743/1983, No. 80848/1985 and No. 94126/1985. Examples of the combined use of the surface active agents of the alkylene oxide type and other compounds are disclosed in, for example, Japanese Unexamined Patent Publications No. 89626/1979, No. 70837/1980, No. 11341/1982, No. 109947/1982, No. 74554/1984, No. 76741/1985, No. 76742/1985, No. 76743/1985, No. 80839/1985, No. 80846/1985, No. 80847/1985, No. 131293/1975 and No. 29715/1978.

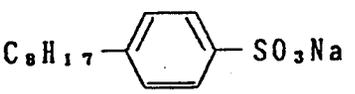
The anionic surface active agents may include those disclosed in Japanese Unexamined Patent Publication No. 21922/1978, GB-1,503,218 and Japanese Patent Publication No. 1617/1981, and sulfates of higher alcohols, higher alkyl sulfonates, alkylbenzene sulfonates, dialkyl sulfosuccinates, acylmethyltauride, N-acylsarcocinate, aliphatic monoglyceride sulfate and α-sulfonic acid.

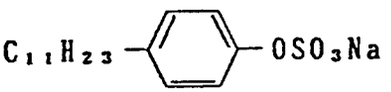
The fluorine-containing surface active agents may include the compounds disclosed in Japanese Patent Publications No. 9303/1972, No. 43130/1973, No. 25087/1977 and No. 1230/1982, Japanese Unexamined Patent Publications No. 46733/1974, No. 16525/1975, No. 34233/1975, No. 32322/1976, No. 14224/1979, No. 111330/1979, No. 557762/1980, No. 19042/1981, No. 41093/1981, No. 34856/1981, No. 11341/1982, No. 29691/1982, No. 64228/1982, No. 146248/1982, No. 114944/1981, No. 114945/1981, No. 196544/1983, No. 200235/1983, No. 109548/1985 and No. 136534/1982, US Patent No. 3,589,906, No. 3,775,126, and No. 4,292,402, RD-16630, and Japanese Unexamined Patent Publication No. 164738/1985.

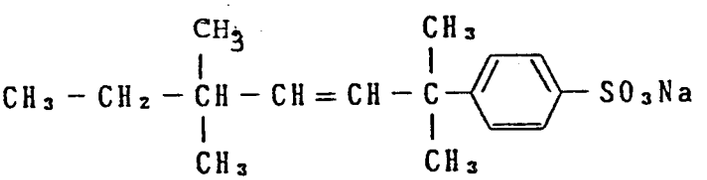
The surface tension of the coating solutions regulated by the surface active agent can be determined by measurement according to the Wilhelm's conventional method at a prescribed liquid temperature.

Preferred anionic surface active agents containing no polyalkylene oxide group are:

1 − 1 $C_4H_9O-SO_3Na$

1 − 2 

1 − 3 

1 − 4 

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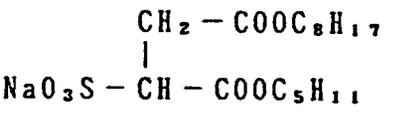

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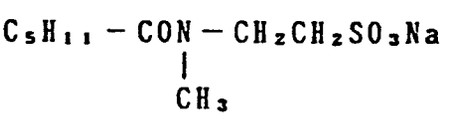

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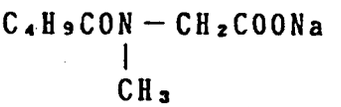

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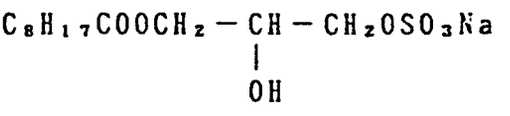

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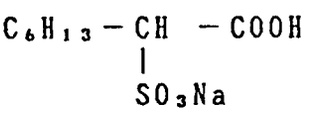

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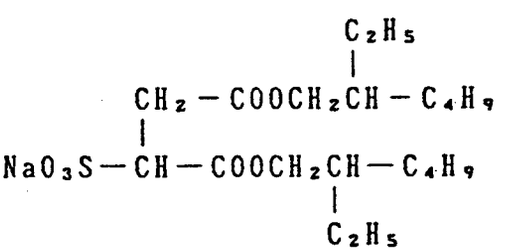


Preferred fluorine-containing surface active agents are:

2 − 1 $C_3F_5O(CH_2CH_2O)_{20}C_{12}H_{25}$

2 − 2 $C_3F_5O(CH_2CH_2O)_5C_3F_5$

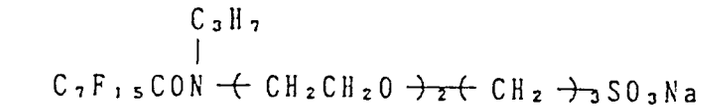
2 − 3 $C_6F_{13}O(CH_2CH_2O)_{10}C_4H_9$

2 − 4 $C_6F_{13}O(CH_2CH_2O)_{20}C_6H_{13}$

2 − 5 $C_6F_{13}O(CH_2CH_2O)_7CH_3$

2 − 6 $C_9F_{17}O(CH_2CH_2O)_{20}CH_3$

2 − 7



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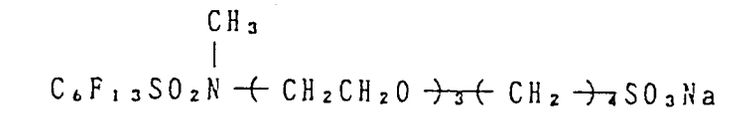

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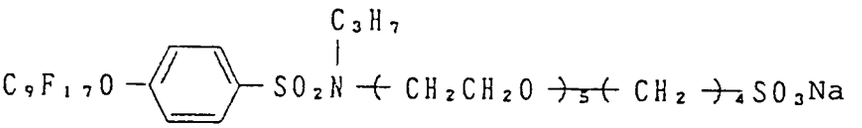

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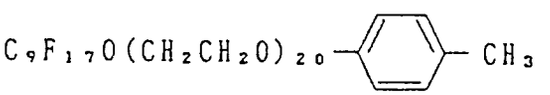

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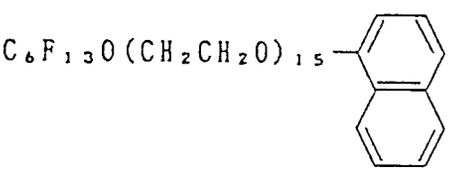

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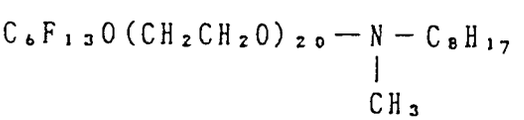

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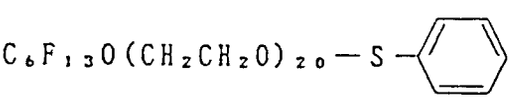


2 − 14 $C_6F_{13}O(CH_2CH_2O)_{40}-C_{18}H_{35}$

2 − 15 $C_9F_{17}O(CH_2CH_2O)_{10}-H$

2 − 16 $C_{12}F_{23}O(CH_2CH_2O)_{50}-CH_3$

2 − 17 $C_6F_{11}O(CH_2CH_2O)_{20}(CHCH_2O)_3CH_3$ (CH$_3$ on the CHCH$_2$O unit)

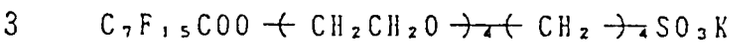
2 − 18 $C_{10}F_{12}CH_2CH(OH)CH_2O(CH_2CH_2O)_{20}-C_6H_4-C_9H_{19}$

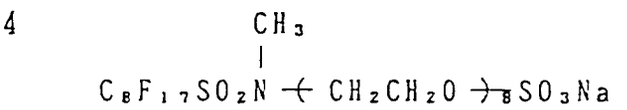
2 − 19 $C_9F_{19}CH_2CH(OH)CH_2O(C_2H_4O)_{10}CH_3$

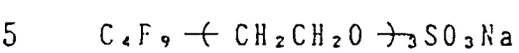
2 − 20 $C_6F_{13}SO_2N(C_3H_7)-(CH_2CH_2O)_2C(=O)-CH$ and $C_6F_{13}SO_2N(C_3H_7)-(CH_2CH_2O)_2C(=O)-CH_2-SO_3Na$

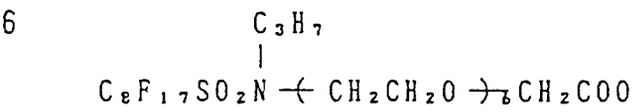
2 − 21 $C_8F_{17}(CH_2CH_2O)_5(CH_2)_4SO_3Na$

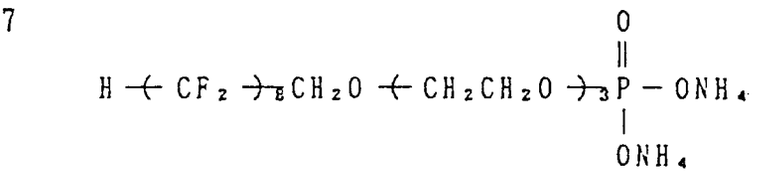
2 − 22 $H(CF_2)_8CH_2O(CH_2CH_2)_4(CH_2)_3SO_3H$

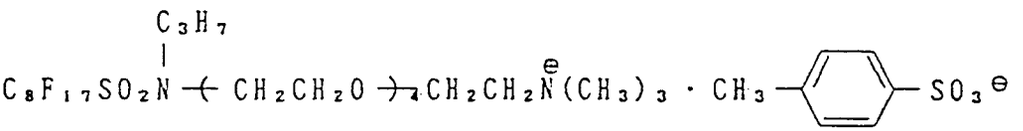
2 − 23 

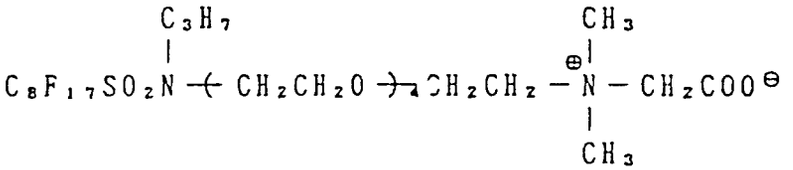
2 − 24 

2 − 25 

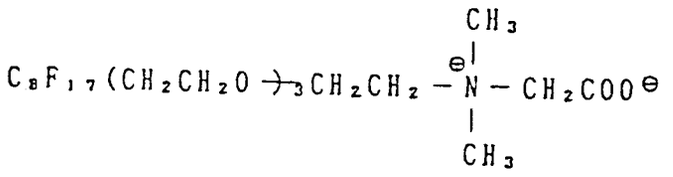
2 − 26 

2 − 27 

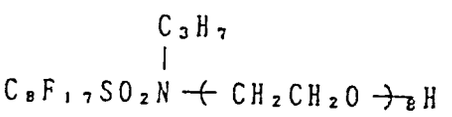
2 − 28 

2 − 29 

2 − 30



2 − 31



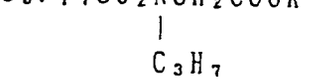
2 − 32 $C_6F_{13}SO_3Na$

2 − 33 $C_8F_{17}SO_3Na$

2 − 34 $C_6F_{13}COOK$

2 − 35 $C_8F_{17}SO_3COOK$

2 − 36



2 − 37 $F_3C-(CF_2)_2-COOH$

2 − 38 $H-(CF_2)_6-COOH$

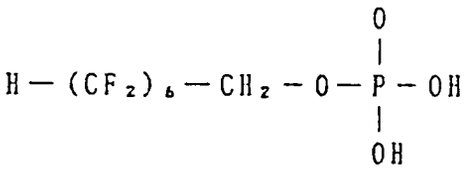
2 − 39 $CF_3-(CF_2)_6-COONH_4$

2 − 40 $H-(CF_2)_{10}-COOH$

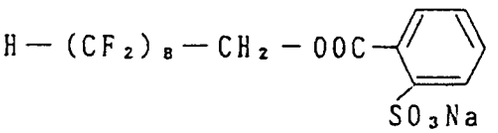
2 − 41 $H-(CF_2)_6-CH_2-OSO_3Na$

2 − 42 $H-(CF_2)_3-CH_2-OSO_3Na$

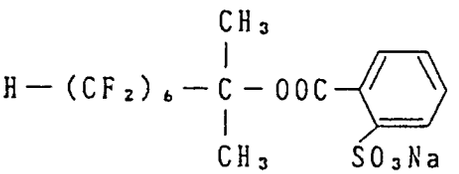
2 − 43



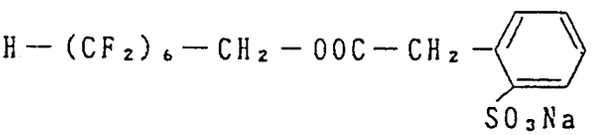
2 − 44



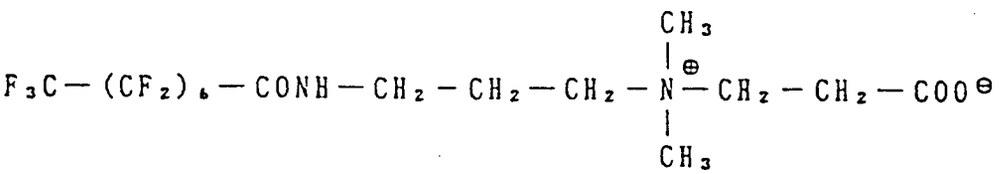
2 − 45



2 − 46

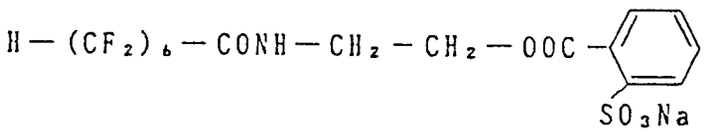


2 − 47

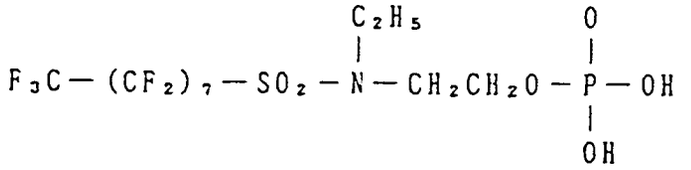


2 − 48 $H-(CF_2)_6-CONH-CH_2-O-SO_3Na$

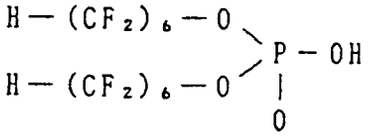
2 − 49



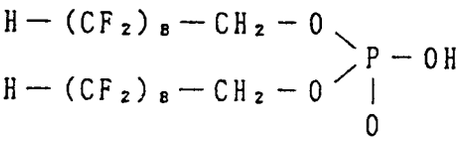
2 − 50



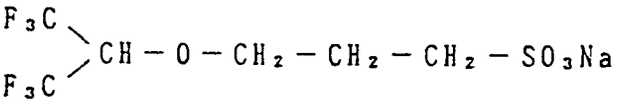
2 − 51



2 − 52



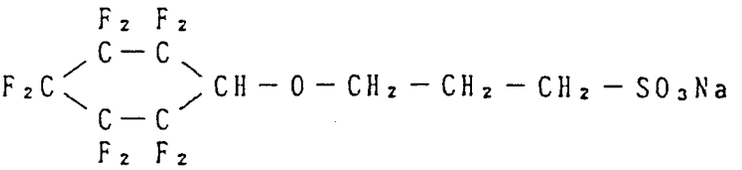
2 − 53



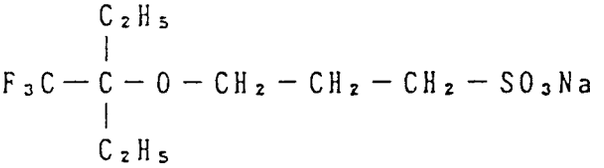
2 − 54 $H-(CF_2)_6-CH_2-O-CH_2-CH_2-CH_2-SO_3Na$

2 − 55 $F_3C-(CF_2)_6-CH_2-O-CH_2-CH_2-CH_2-SO_3Na$

2 − 56



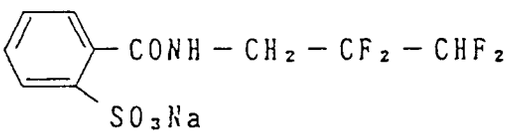
2 − 57



2 − 58 $F_3C-(CF_2)_2-COO-CH_2-CH_2-CH_2-SO_3Na$

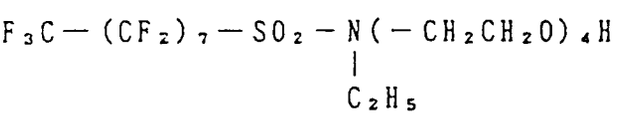
2 − 59 $H-(CF_2)_{10}-COO-CH_2-CH_2-CH_2-SO_3Na$

2 − 60



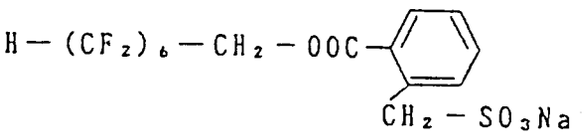
2 − 61 $F_3C-(CF_2)_2-COO(-CH_2CH_2O)_7-CH_3$

2 − 62

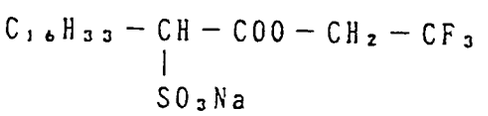


2 − 63 $F_3C-(CF_2)_2-CH_2O(-CH_2CH_2O)_5H$

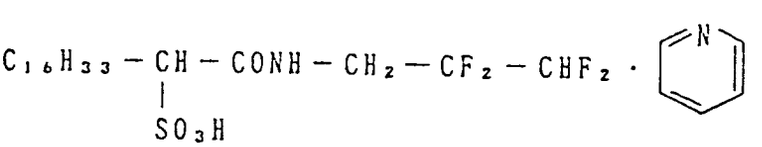
2 - 64



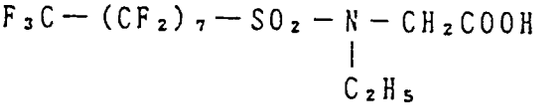
2 - 65



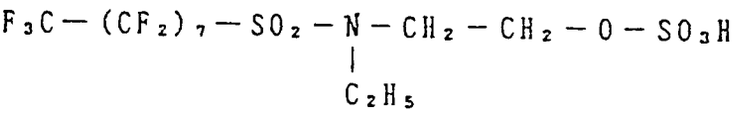
2 - 66



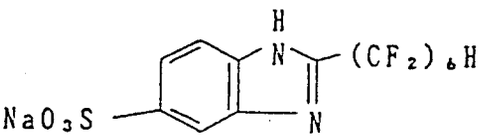
2 - 67



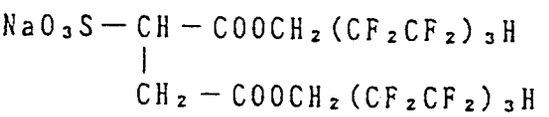
2 - 68



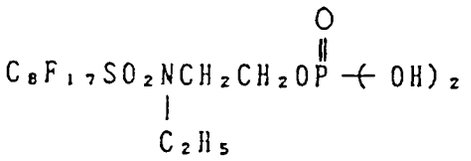
2 - 69



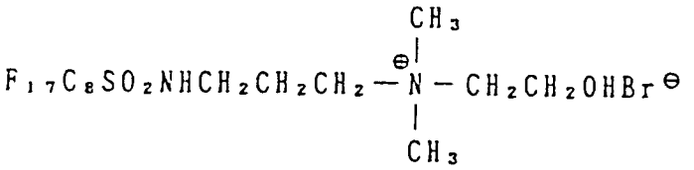
2 - 70



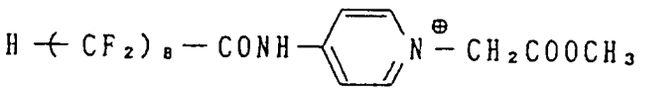
2 - 71



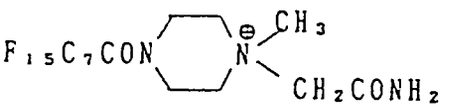
2 - 72



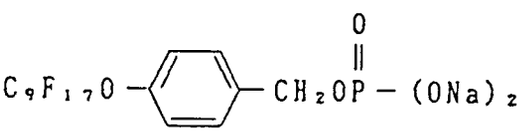
2 - 73



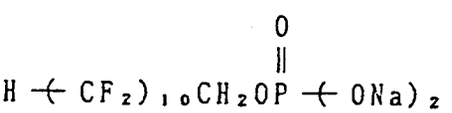
2 - 74



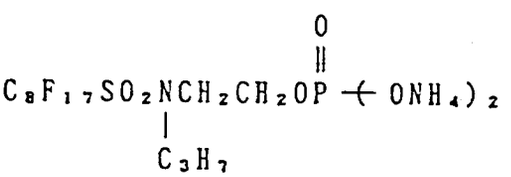
2 - 75



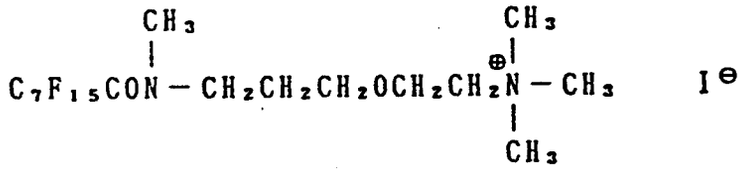
2 - 76



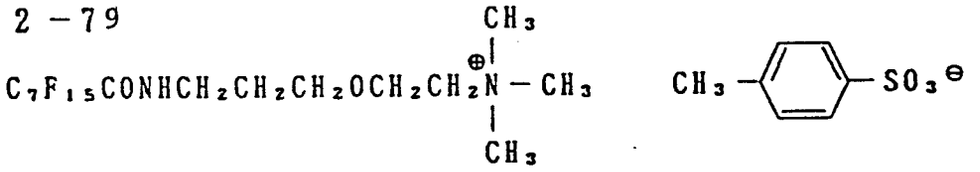
2 - 77



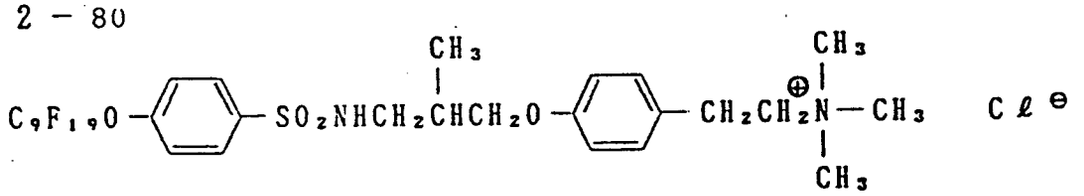
2 − 78



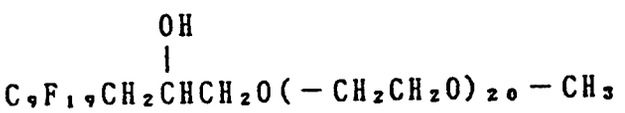
2 − 79



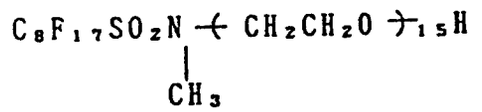
2 − 80



2 − 81



2 − 82



Commercially available fluorine-containing surface active agents include UNIDAIN (trade mark) from Daikin Industries, Ltd. and FLOLARD (trade mark) from 3M (Sumitomo 3M Limited).

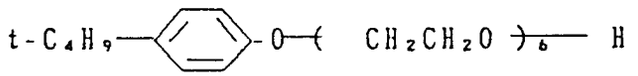
Specific examples of polyoxyethylene surface active agents preferably used in this invention are:

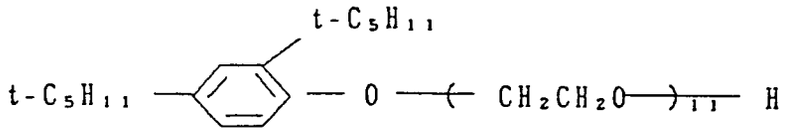
3-1 $C_{11}H_{23}COO\text{-}(CH_2CH_2O)_{8}\text{-}H$

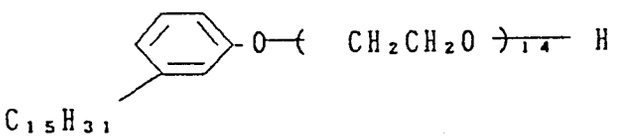
3-2 $C_{17}H_{33}COO\text{-}(CH_2CH_2O)_{15}\text{-}H$

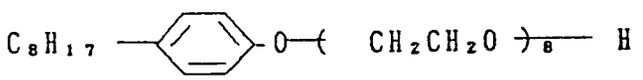
3-3 $C_8H_{17}O\text{-}(CH_2CH_2O)_{7}\text{-}H$

3-4 $C_{22}H_{45}O\text{-}(CH_2CH_2O)_{25}\text{-}H$

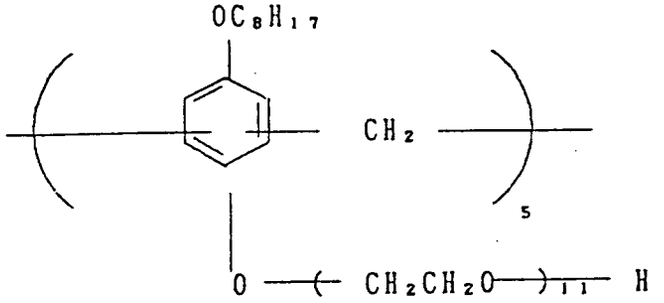
3-5 

3-6 

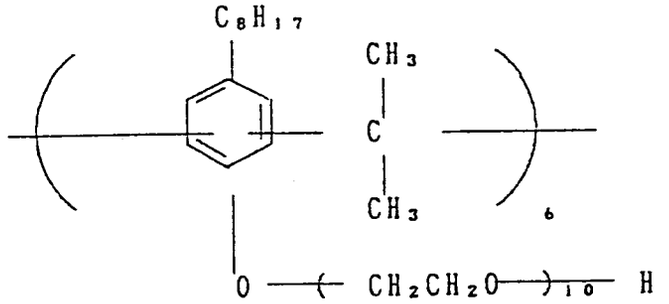
3-7 

3-8 

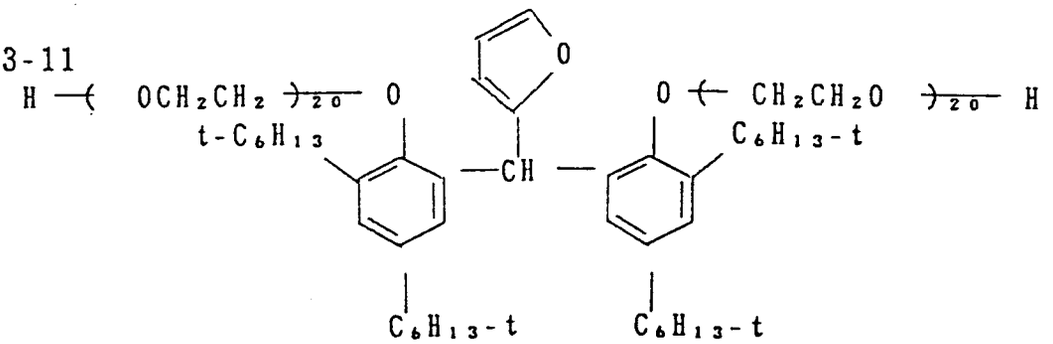
3-9



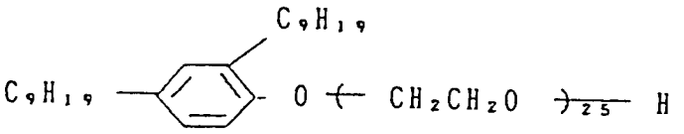
3-10



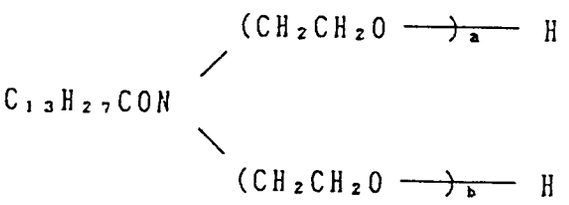
3-11



3-12

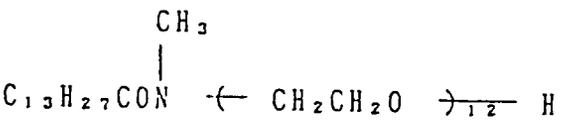


3-13

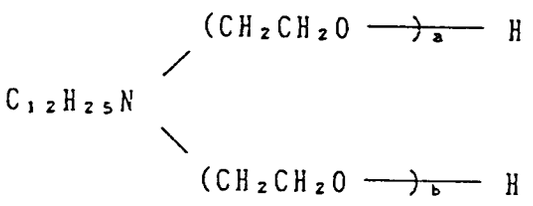


a + b = 1 5

3-14

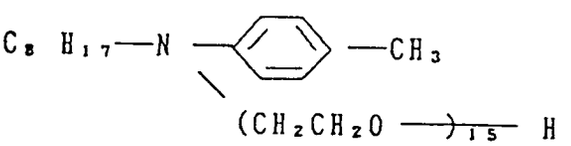


3-15



a + b = 2 0

3-16



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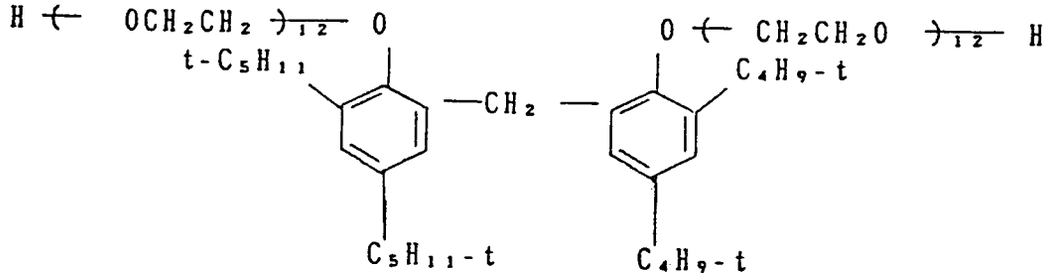

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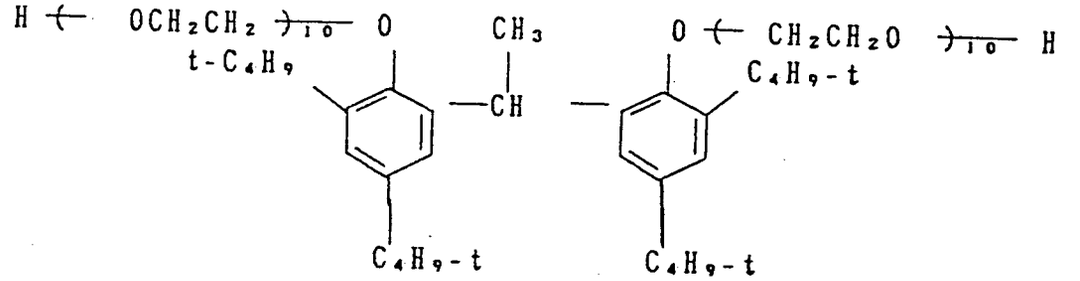
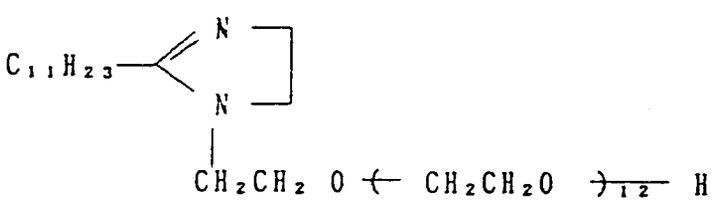


3-19 $C_{12}H_{23}S$ —(CH_2CH_2O)$_{16}$ H

3-20 $C_{12}H_{25}O$ —($CH(CH_3)CH_2O$)$_3$ —(CH_2CH_2O)$_{15}$ H

3-21



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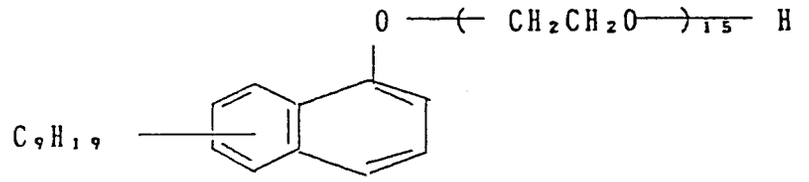

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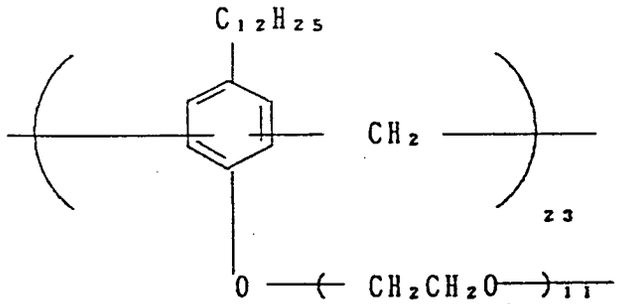

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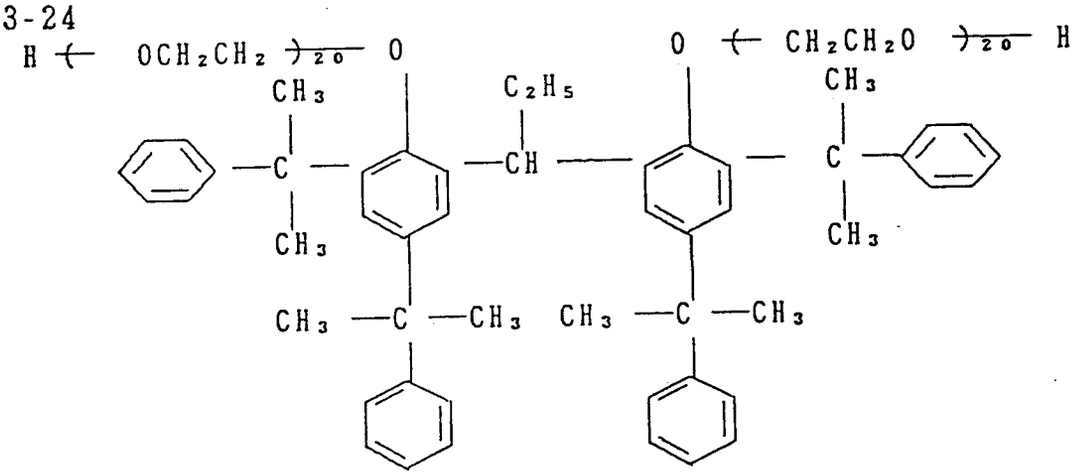

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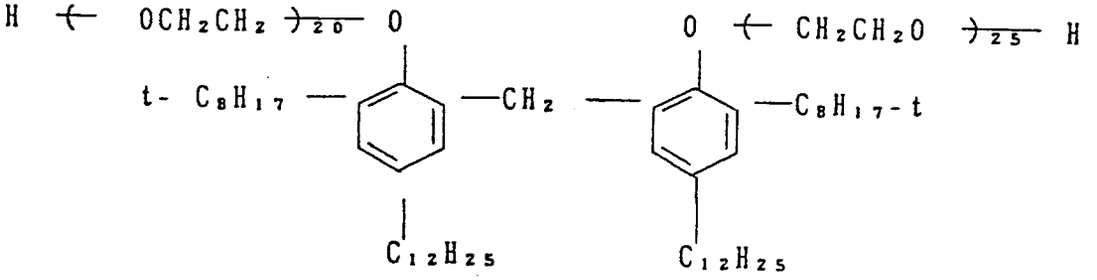

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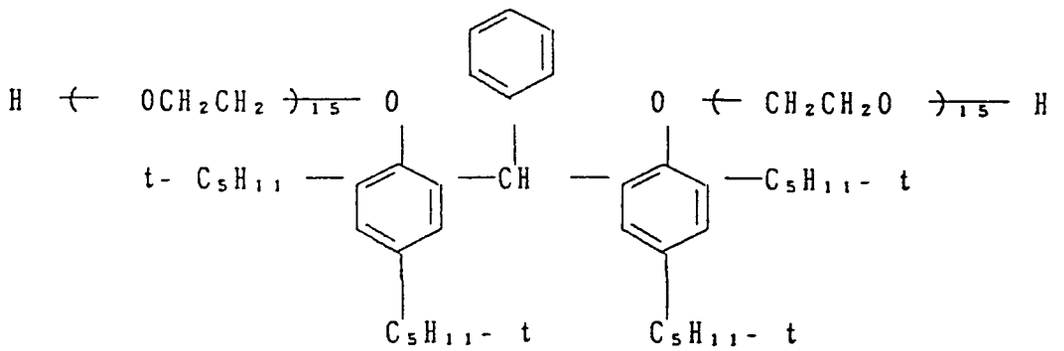

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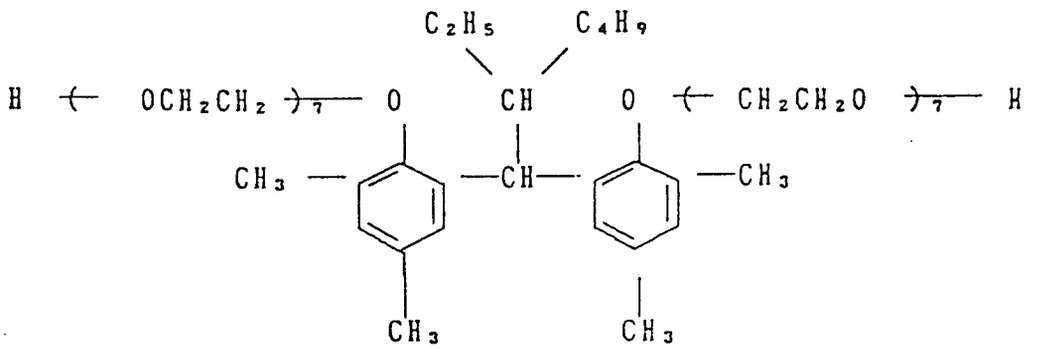

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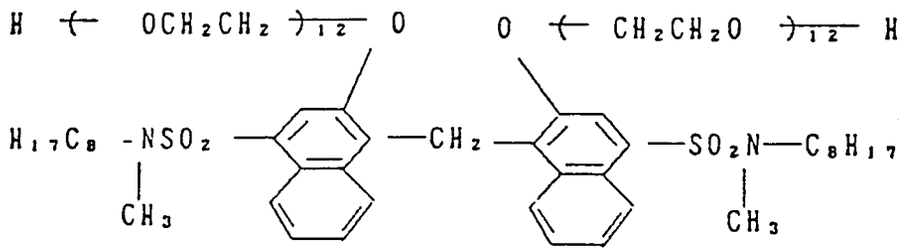

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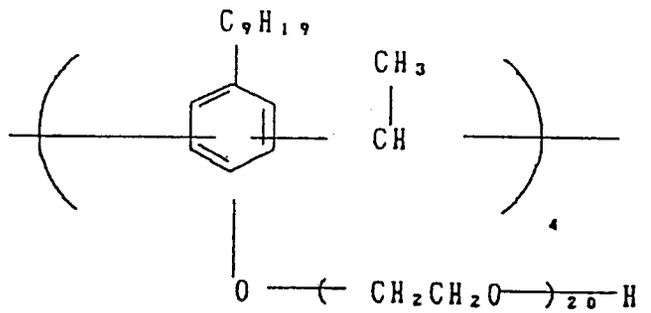

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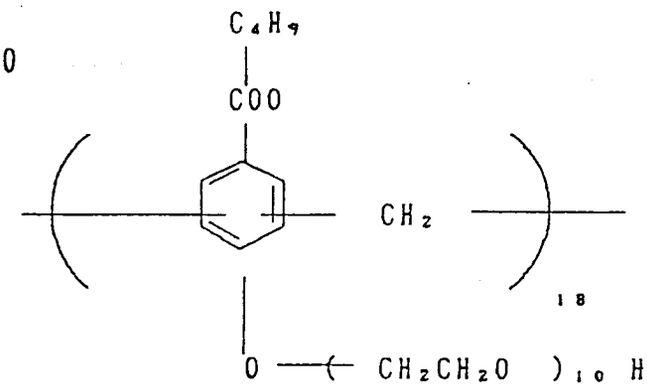

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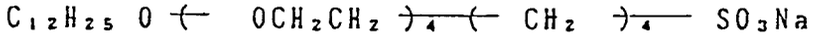

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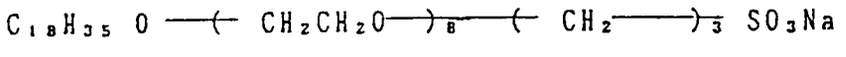

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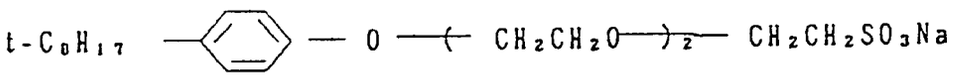

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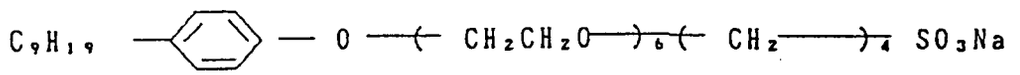

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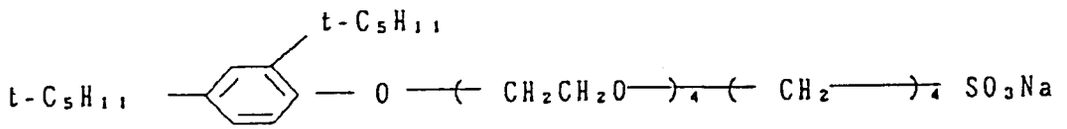

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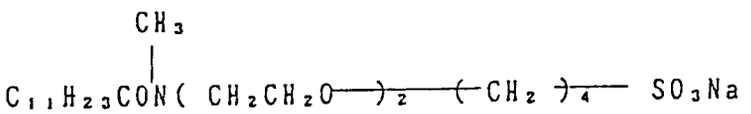

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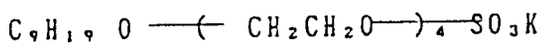

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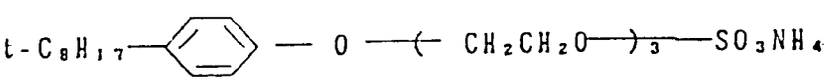

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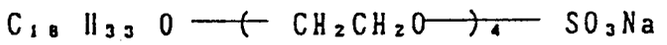

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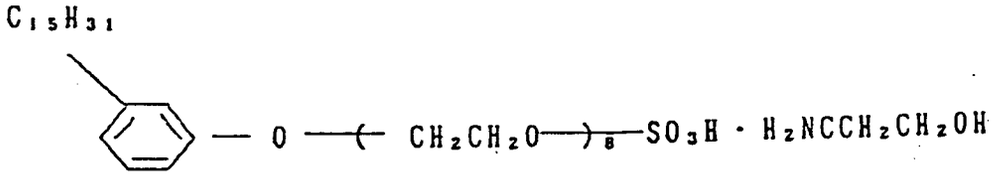

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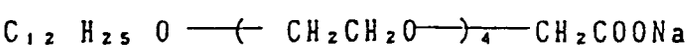

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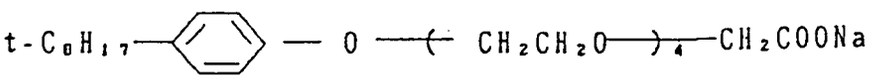

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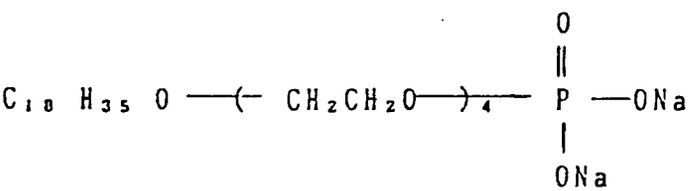

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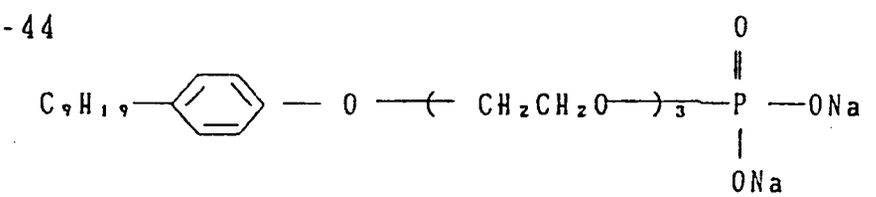
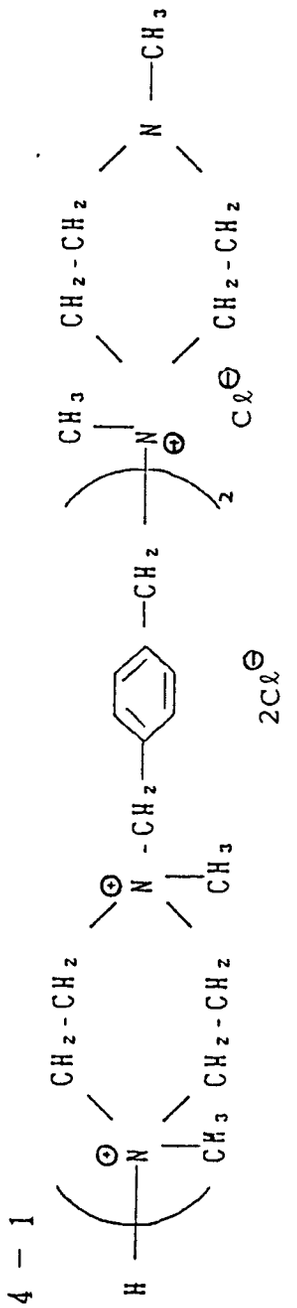
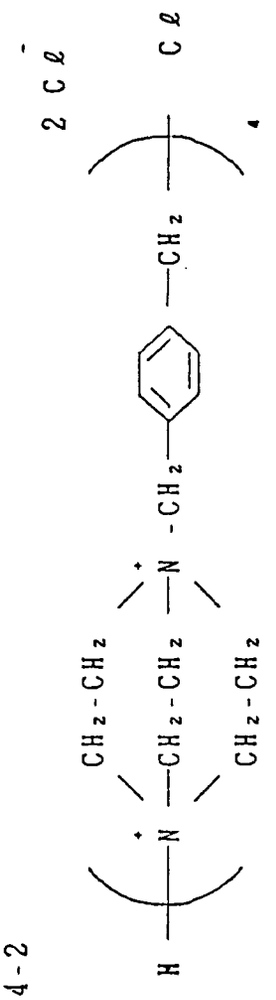


Preferable quaternary ammonium salts may include the compounds shown below as 4-1 to 4-20.



4 - 1



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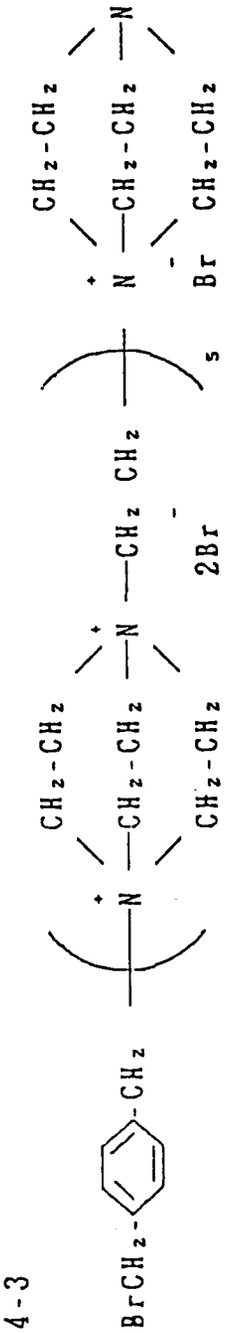
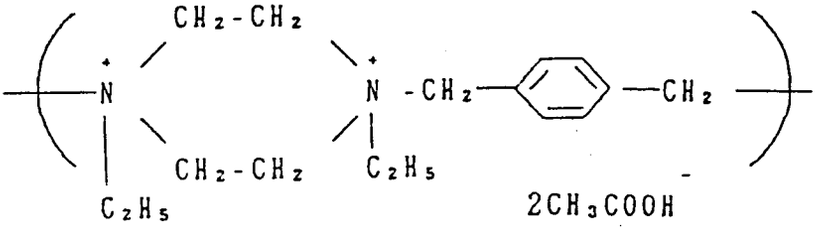


4-3

4-4



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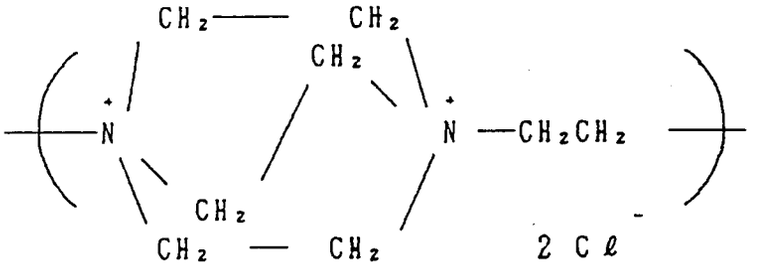

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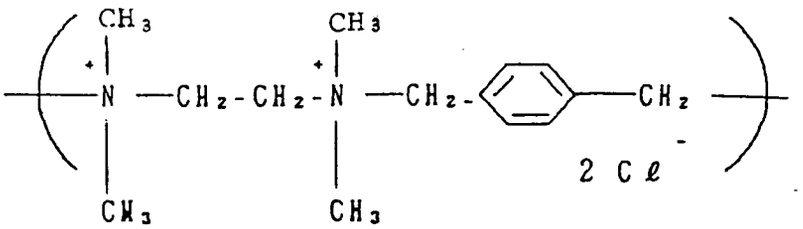

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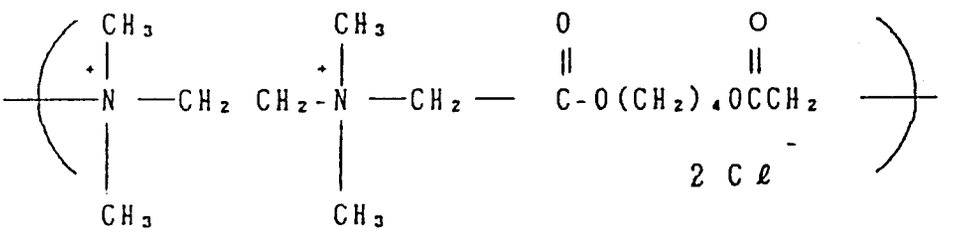

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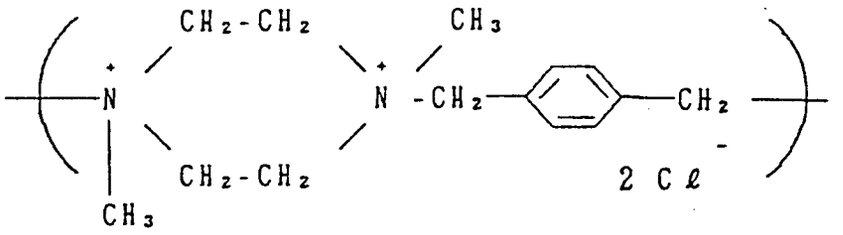

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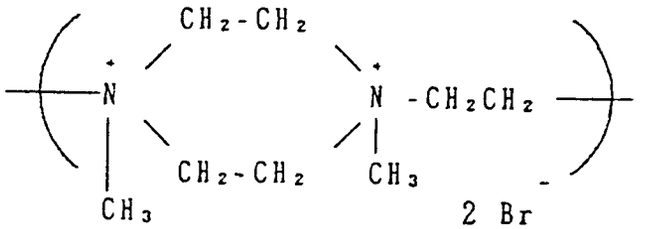

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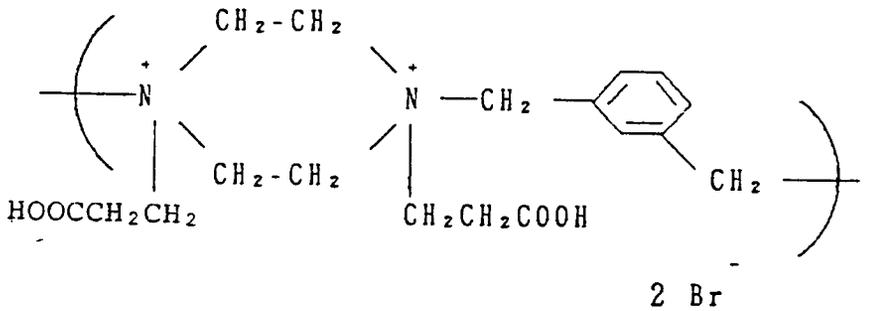

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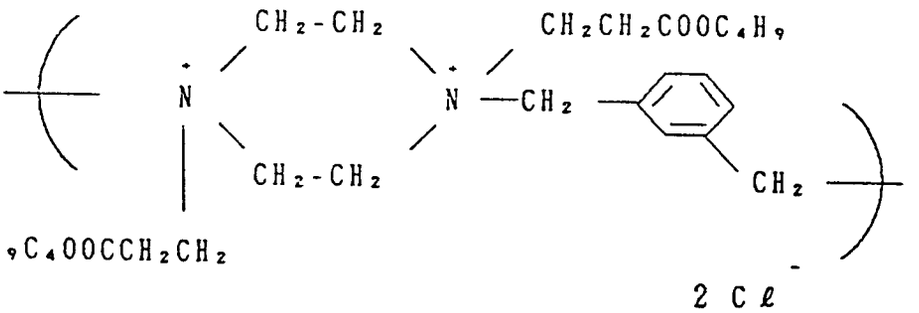

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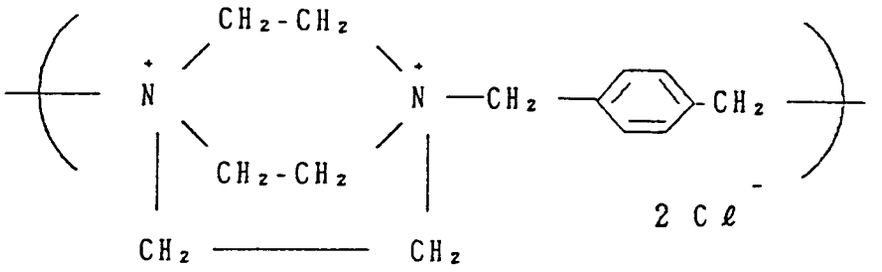

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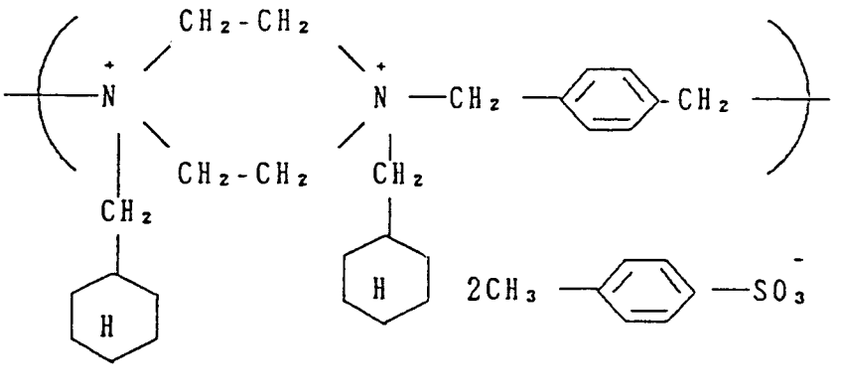

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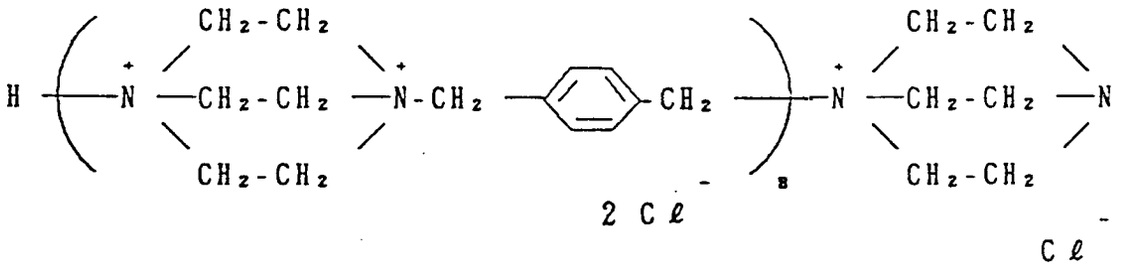

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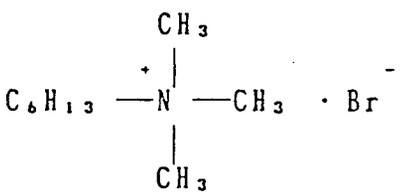

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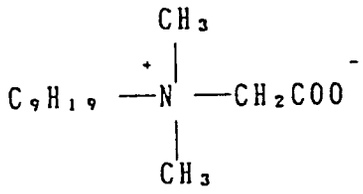

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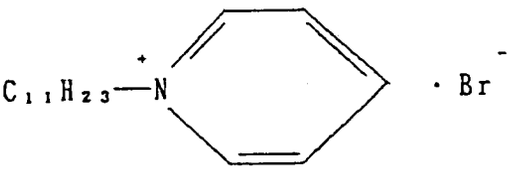

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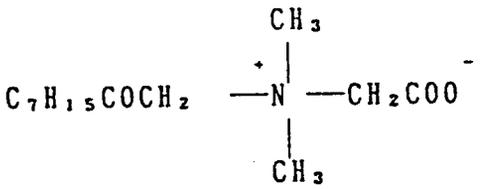

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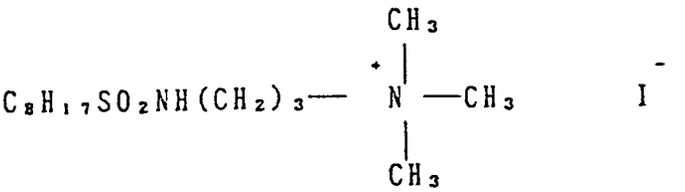

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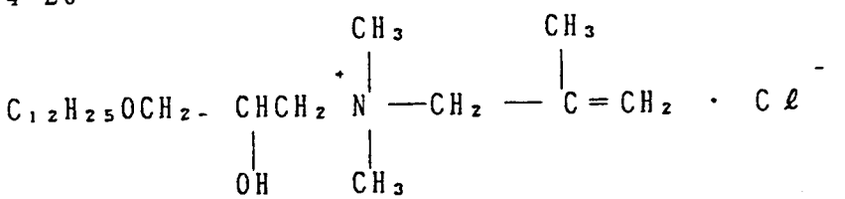


Coating solutions used in embodiment (b) of the invention for the outermost layer and the layer adjacent thereto which form the photographic constituent layers of the light-sensitive material of this invention are now described. The coating solutions preferably have a viscosity of 20×10^{-3} Pas (20 cp) or less, more preferably 15×10^{-3} Pas (15 cp) or less. It is further preferable for the difference in the viscosity between the two solutions to be ± 2×10^{-3} Pas (2 cp). Any thickening agent can be used in the solutions if it has a thickening effect and, at the same time, does not particularly adversely affect the light-sensitive silver halide photographic material.

Generally used thickening agents include aqueous polymers having a sulfuric acid ester group (Japanese Patent Publication No. 21574/1961), dextran and sulfuric acid esters thereof (Japanese Patent Publications No. 11989/1960 and No. 12872/1970), polysaccharides (U.S. Patent No. 3,767,410), polymers

having a sulfonic acid group, a carboxylic acid group or a phosphoric acid group (Japanese Unexamined Patent Publication No. 18687/1983) and colloidal silica (Japanese Unexamined Patent Publication No. 36768/1983). Those which are particularly preferred in this invention are disclosed in Japanese Unexamined Patent publication No. 109947/1982.

One or more thickening agents other than colloidal silica can be used as the thickening agent. In such a case, the amount of the thickening agent is suitably selected depending on the layer(s) to which they are added or the nature of the agent. In summary, it is satisfactory if the viscosity is controlled to 20×10^{-3} Pas (20 cp) or less by using the thickening agent.

After control by the thickening agent, the viscosity can be determined by measurement at a liquid temperature of 35 °C with a viscometer such as a B-type viscometer.

In embodiment (a) of the invention the amount of gelatin contained in the photographic constituent layers formed on the support is from 2.20 to 3.10 g/m^2. If the amount of gelatin is in this range, the sensitivity of the light-sensitive material and the resistance to abrasion blackening can be improved to a greater extent than in the case where gelatin is contained in an amount of more than 3.10 g/m^2. If the amount is less than 2.20 g/m^2, the gelatin can be applied to a support only with difficulty.

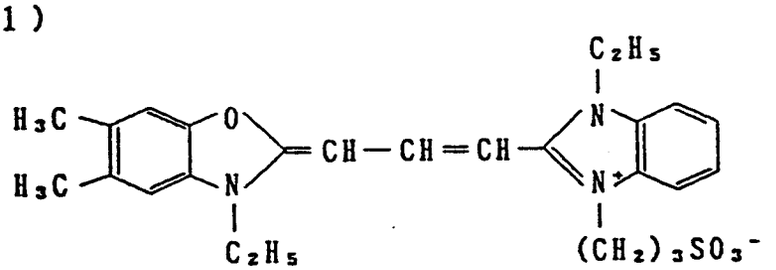
Sensitizing dyes that can be used when working this invention are now described. The sensitizing dyes may be any substances having a desired absorption band in the visible light region; compounds of formulae (I), (II) and (III) as defined above are preferably used.

In Formulae (I), (II) and (III), the carbon ring containing Z_1 and Z_2 is preferably an aromatic ring such as a substituted or unsubstituted benzene ring or naphthalene ring.

In Formula (I), X_1^- may be, for example, a chloride ion, a bromide ion, an iodide ion, a thiocyanate ion, a sulfate ion, a perchlorate ion, a p-toluene sulfonate ion or an ethyl sulfate ion.

Examples of the compound of formula (I) are:

(1)



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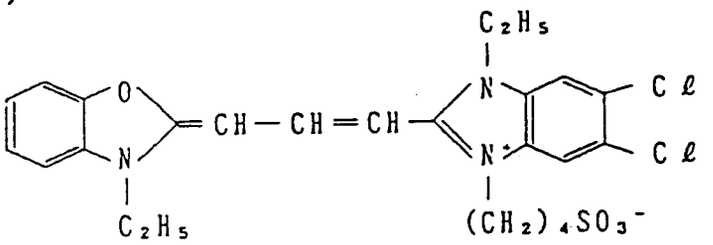

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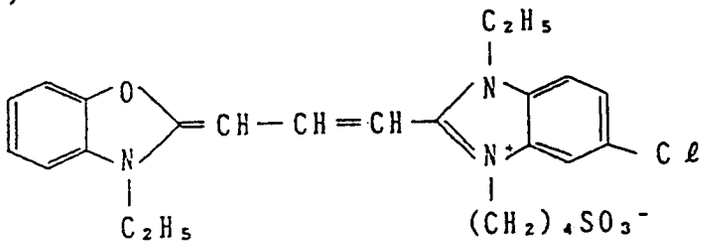

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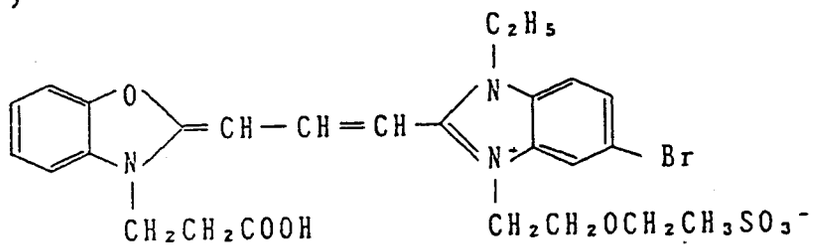

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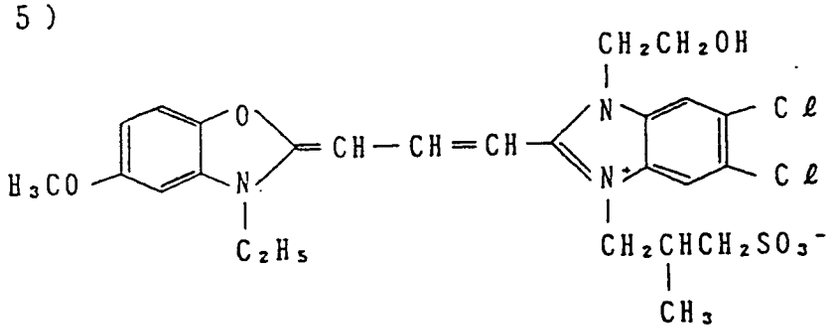

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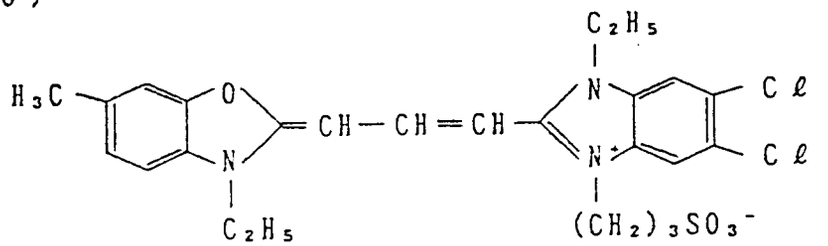

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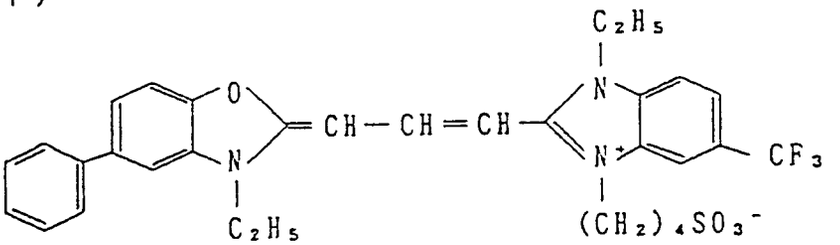

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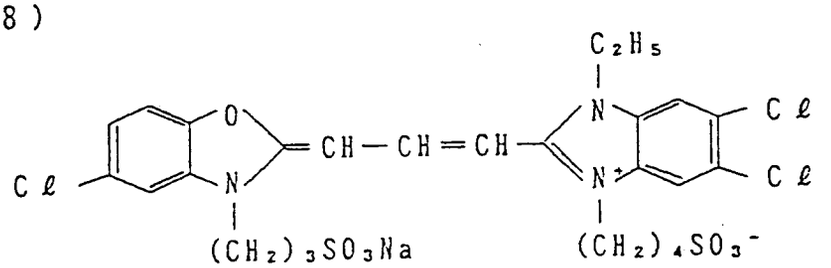

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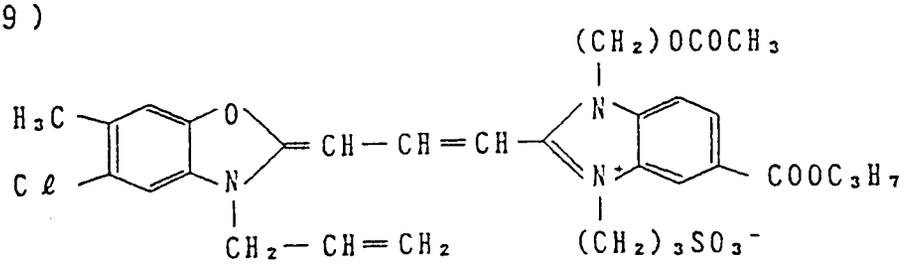

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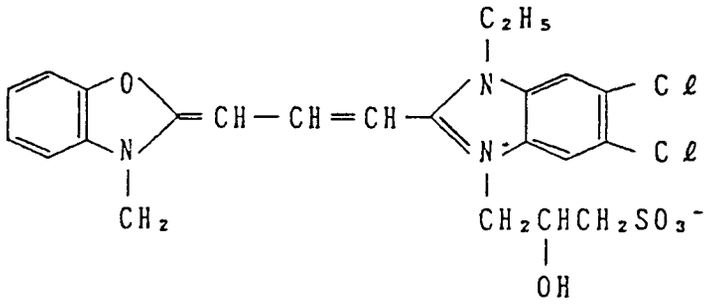

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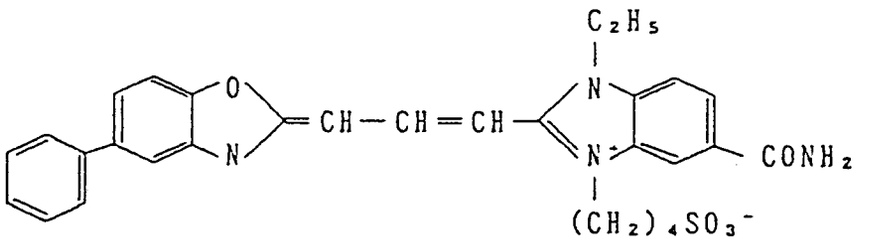

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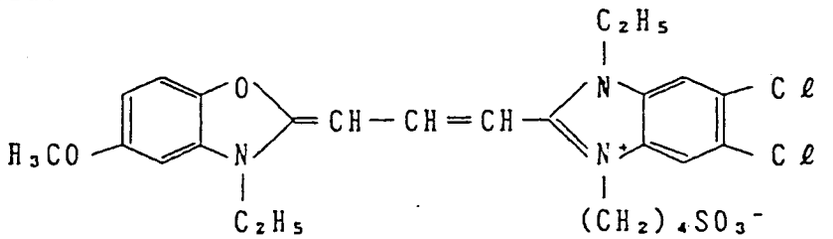

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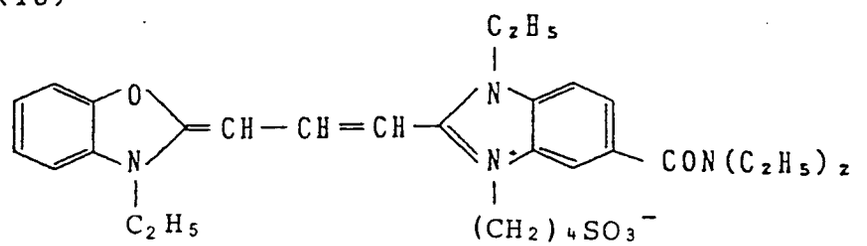

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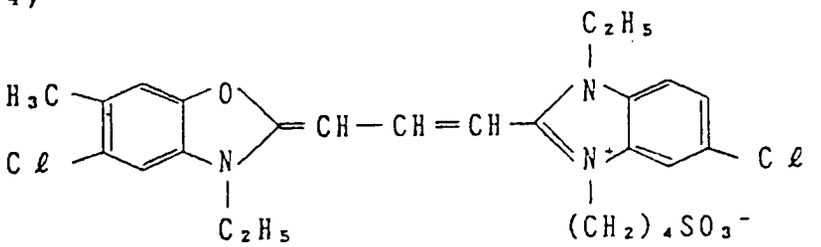

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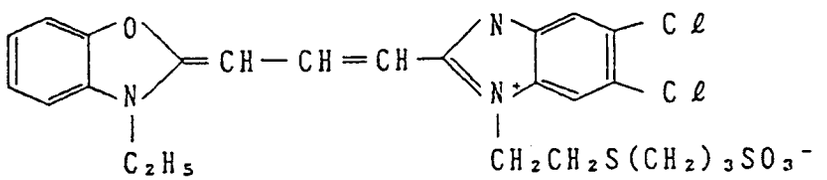

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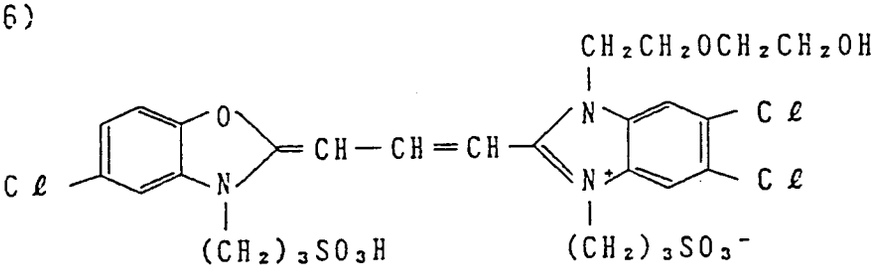

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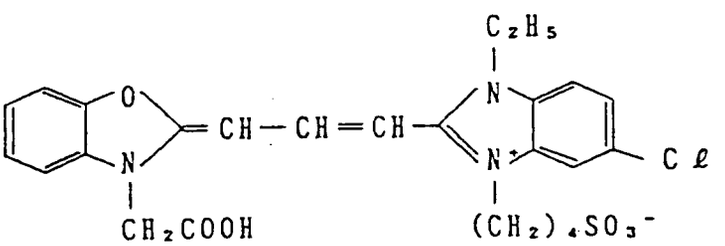

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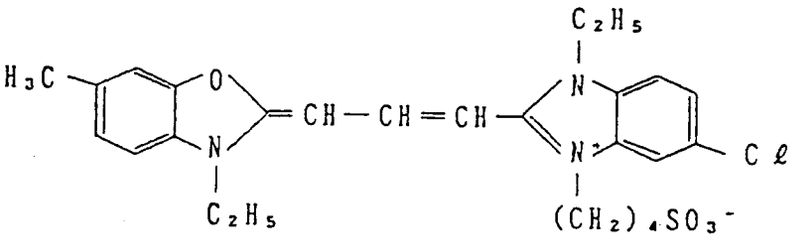

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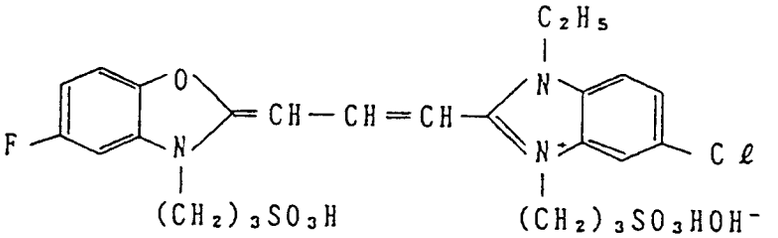

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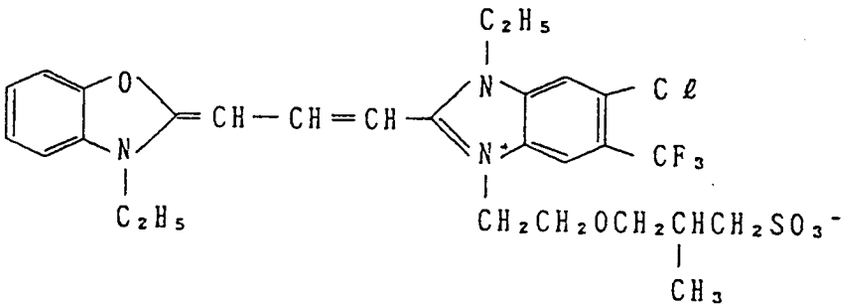

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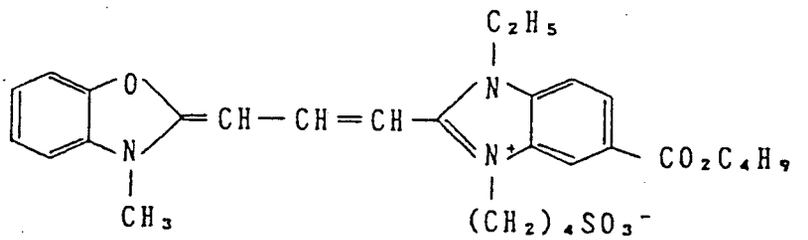

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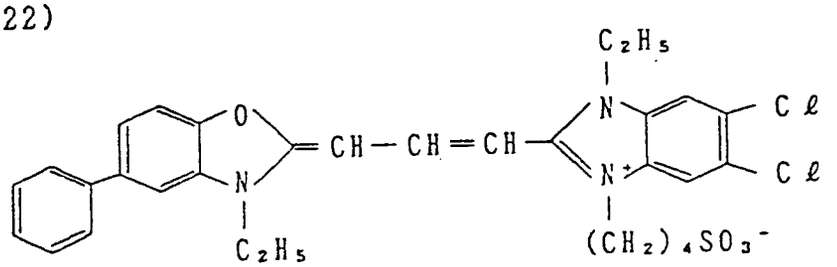

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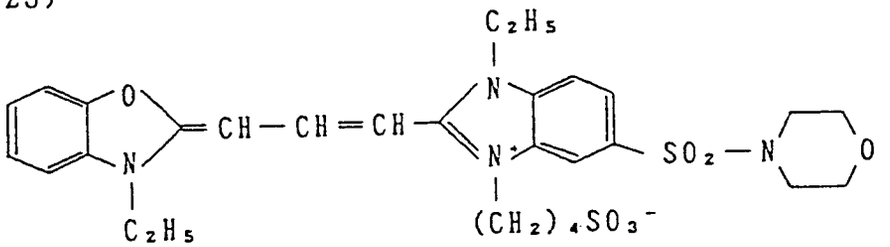

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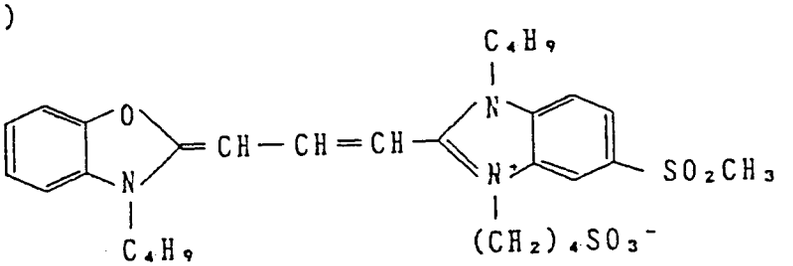

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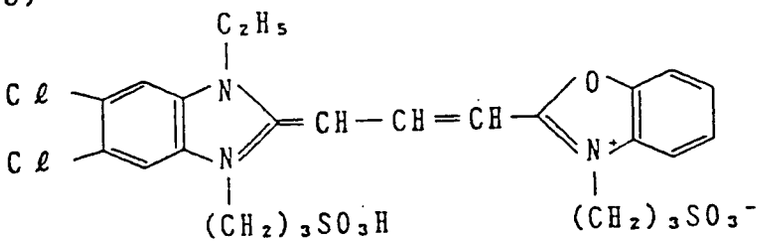

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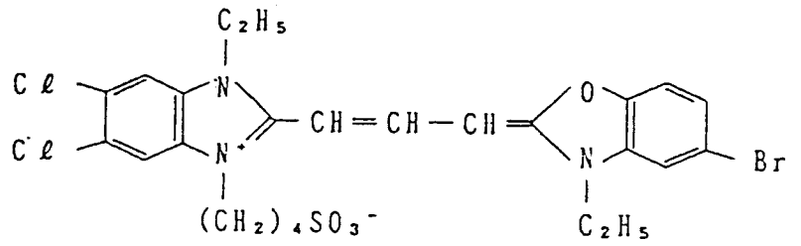

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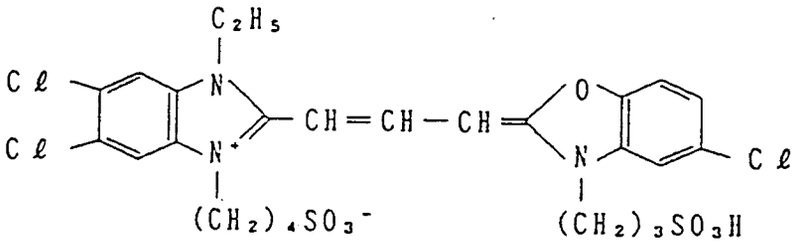

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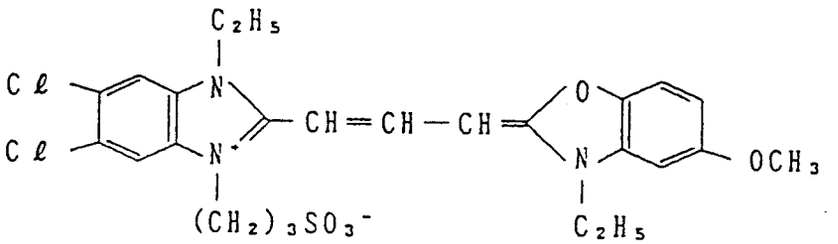

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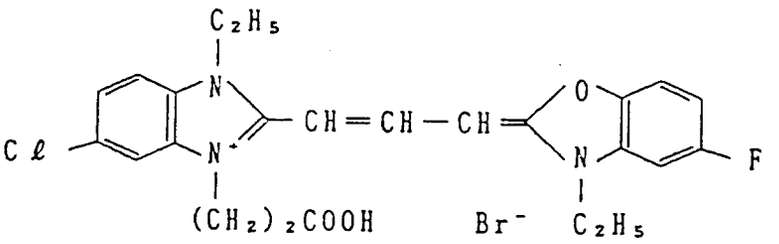

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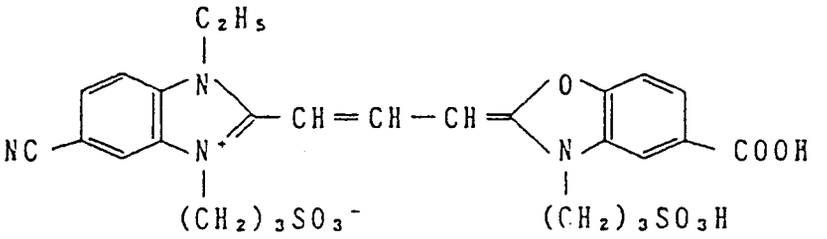

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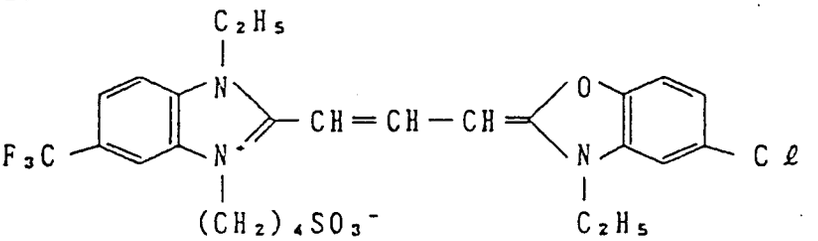

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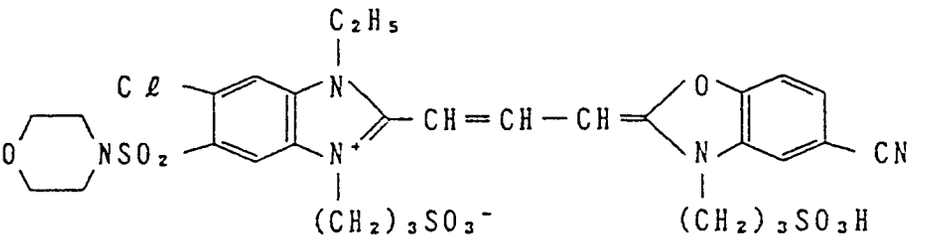

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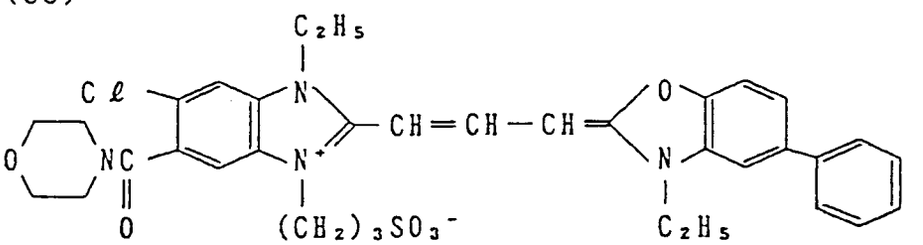

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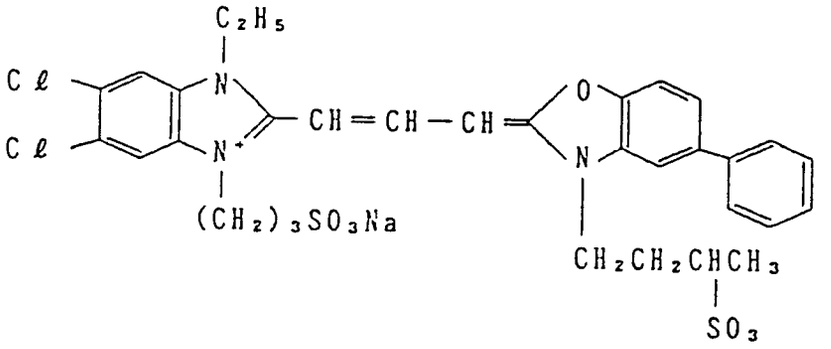

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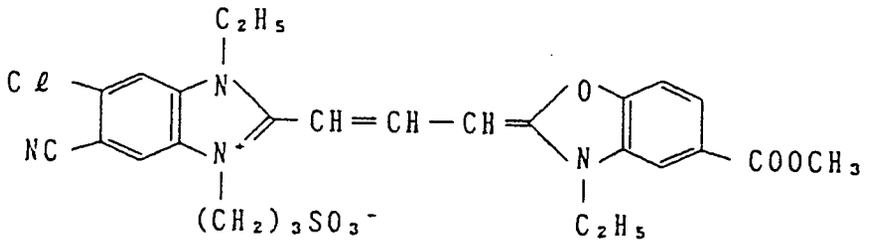

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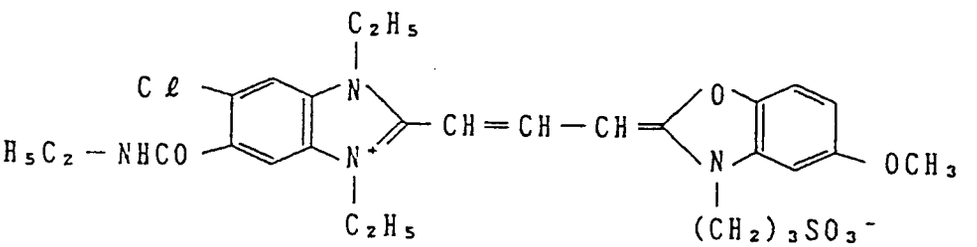

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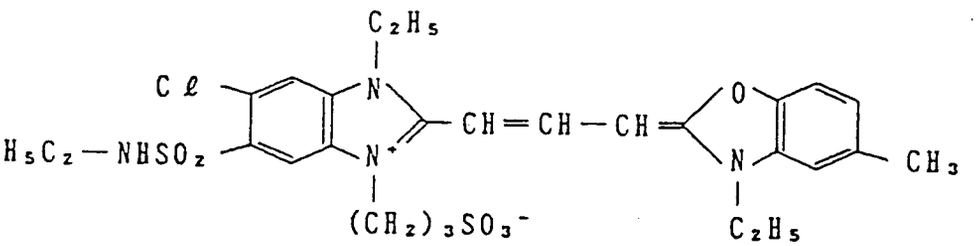

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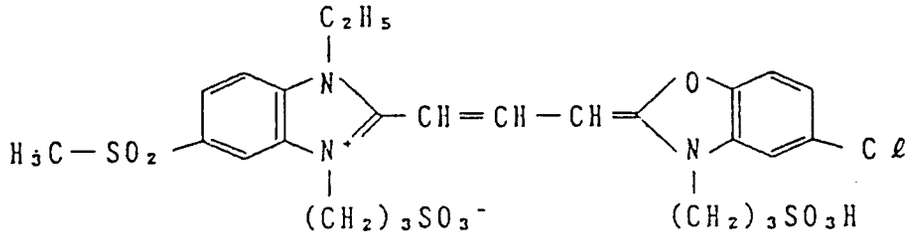

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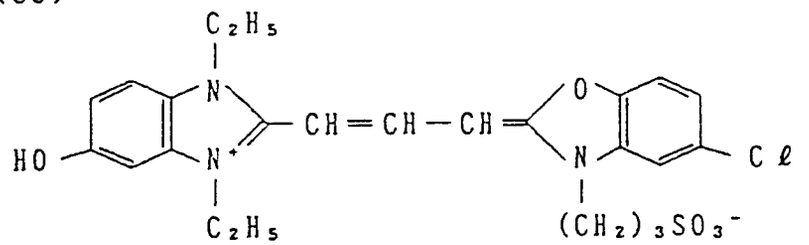

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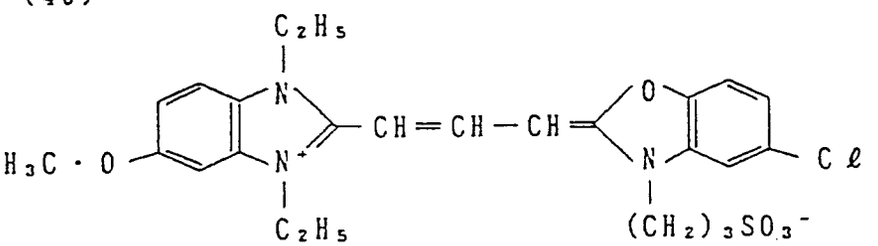

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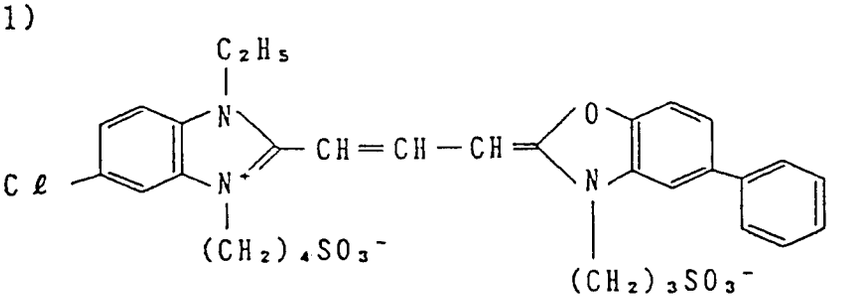
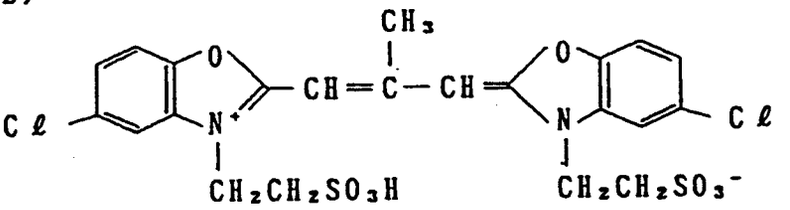


In formula (II) the lower alkyl group represented by R_6 includes, for example, a methyl, ethyl, propyl or butyl group. The aryl group represented by R_6 includes, for example, a phenyl group. The groups represented by R_4 and R_5 include those exemplified for R_1 and R_3 in formula (I). X_2^- may also be an anion exemplified for X_1^- in formula (I).

Examples of the compound of formula (II) are:

(42)



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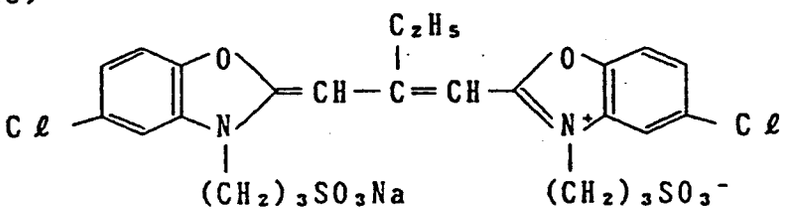

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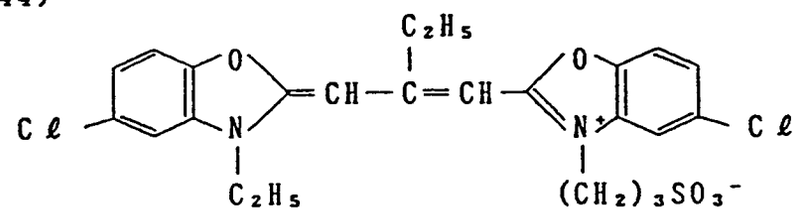

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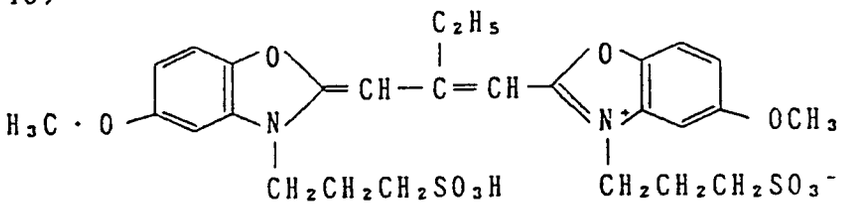

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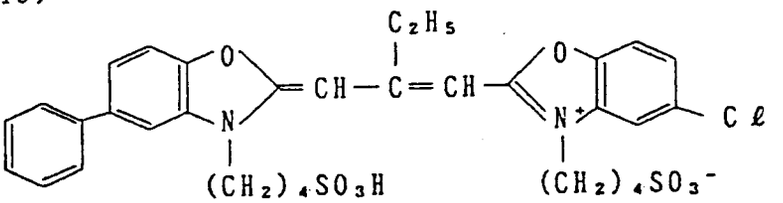

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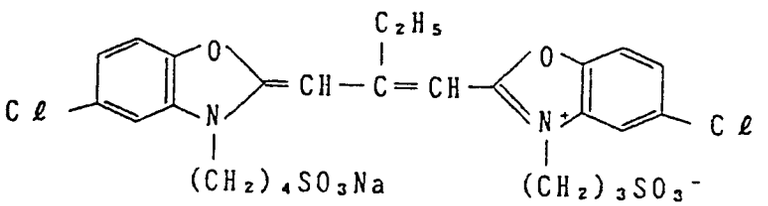

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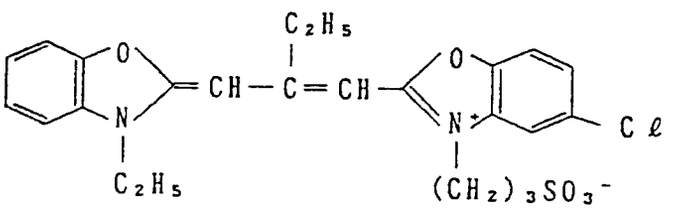

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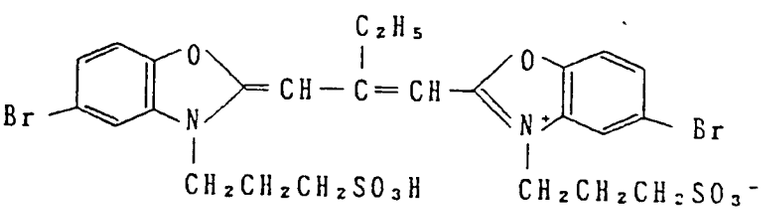

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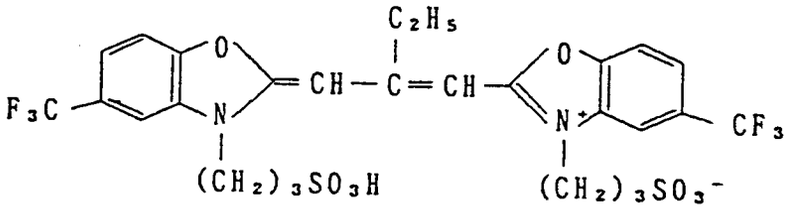

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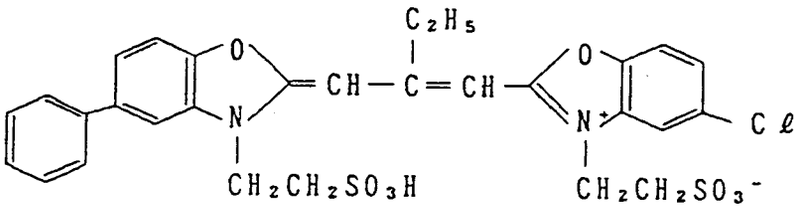

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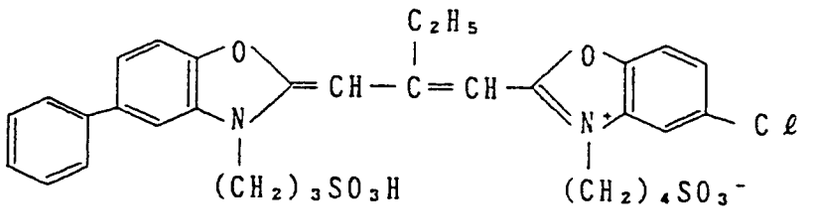

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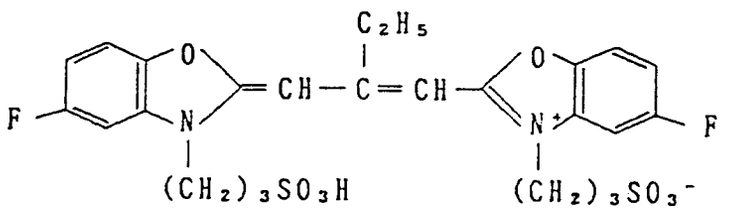

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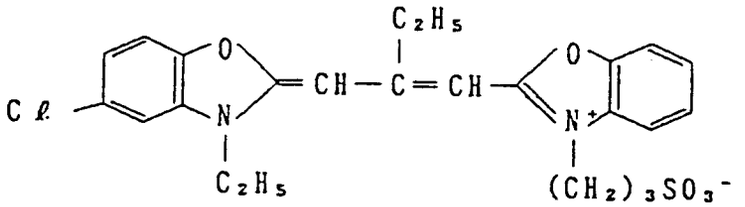

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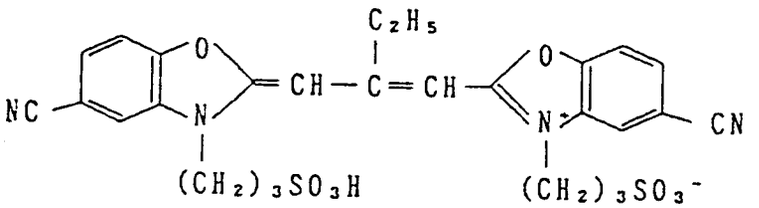

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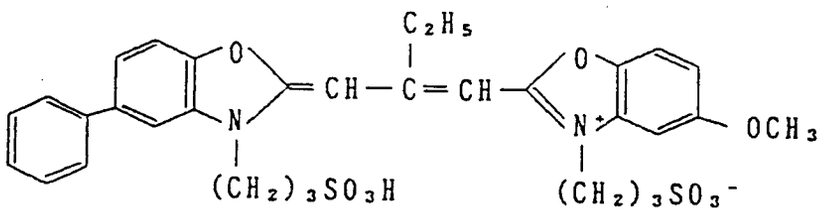

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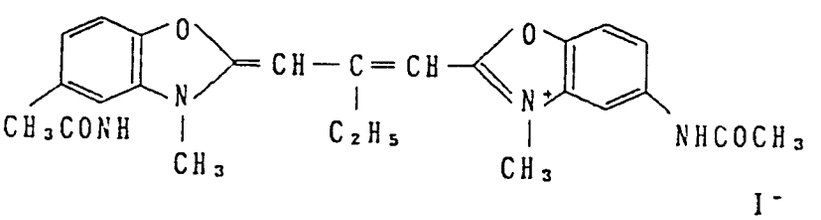

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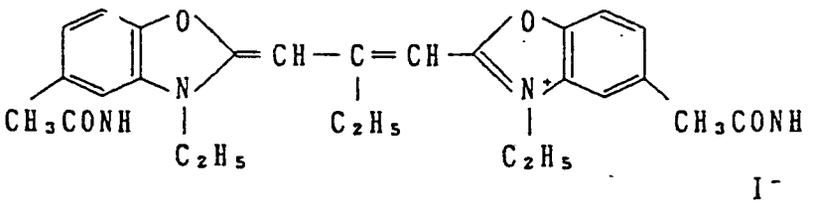

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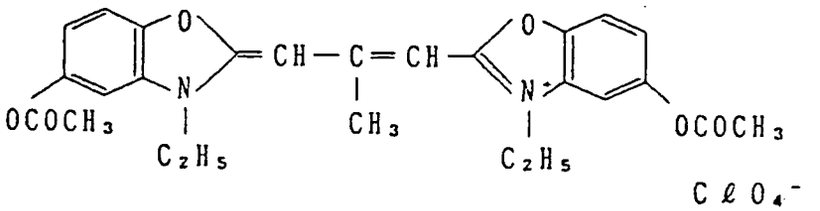

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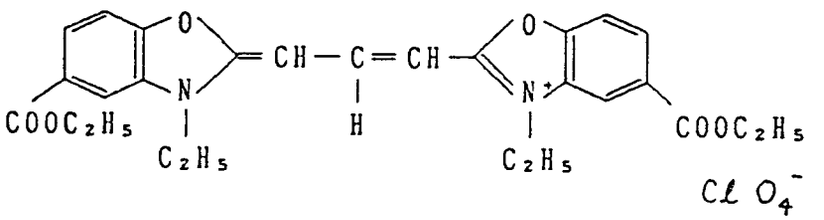

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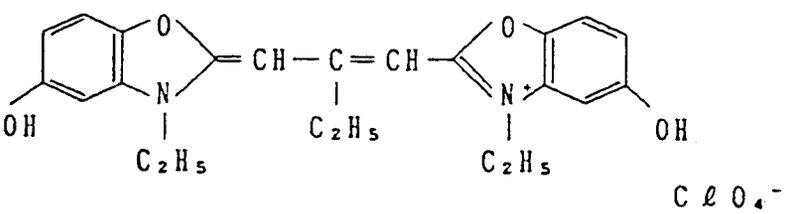

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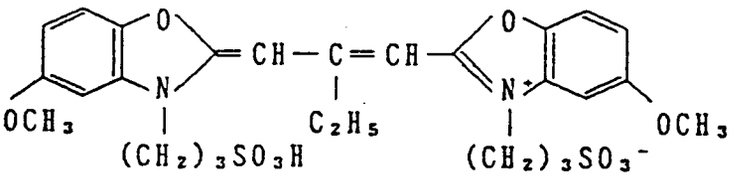

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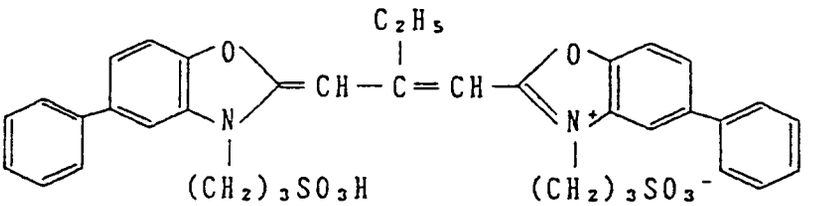

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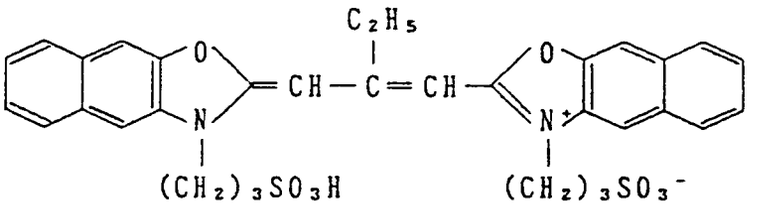

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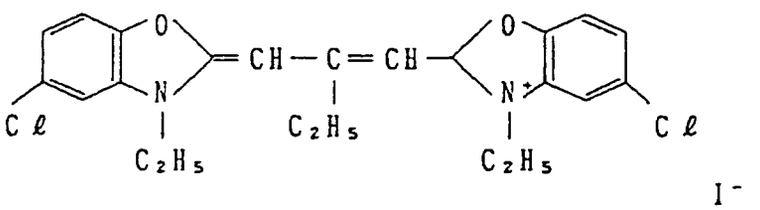
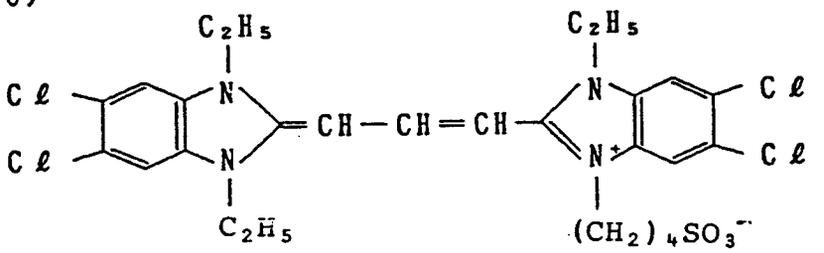


In formula (III), the lower alkyl group represented by R_7 and R_9 includes groups such as methyl, ethyl, propyl and butyl. The substituted alkyl group includes the groups exemplified for R_1 to R_3 in formula (I). The lower alkyl groups represented by R_8 and R_{10} are exemplified by the same groups as for R_7 and R_9. The hydroxyalkyl group, sulfoalkyl group and carboxyalkyl group represented by R_8 and R_{10} include the groups exemplified for R_1 to R_3 in formula (I).

X_3^- may also be an anion exemplified for X_1^- in formula (I).

Examples of the compound of formula (III) are:

(66)



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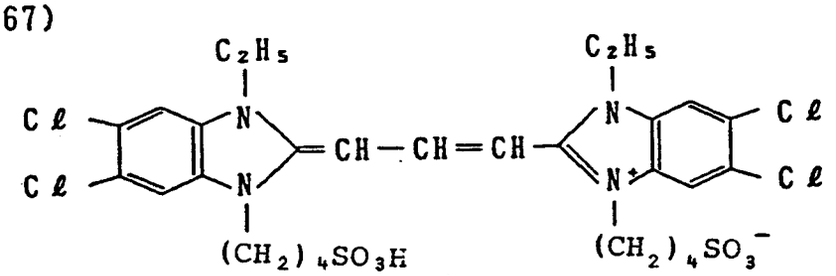

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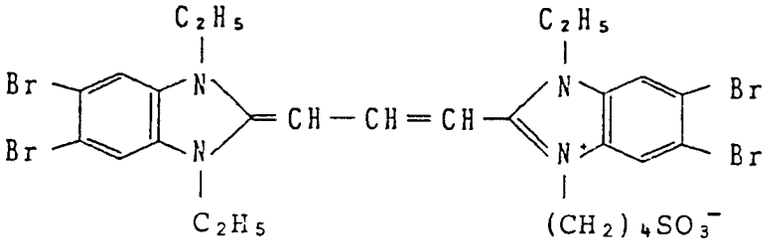

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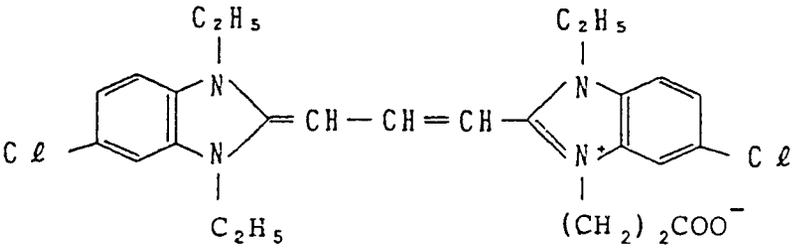

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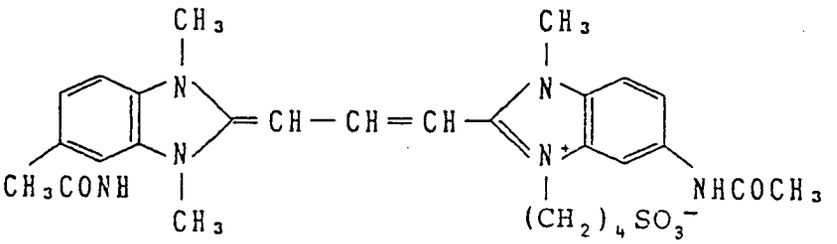

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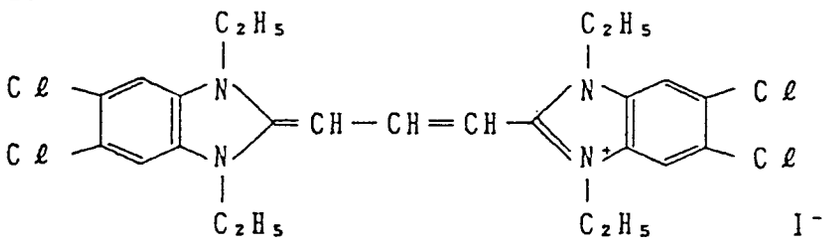

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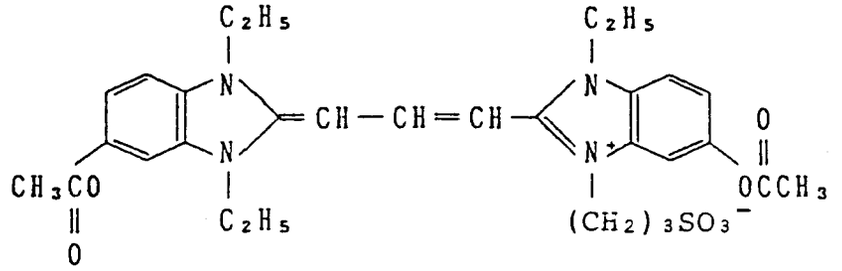

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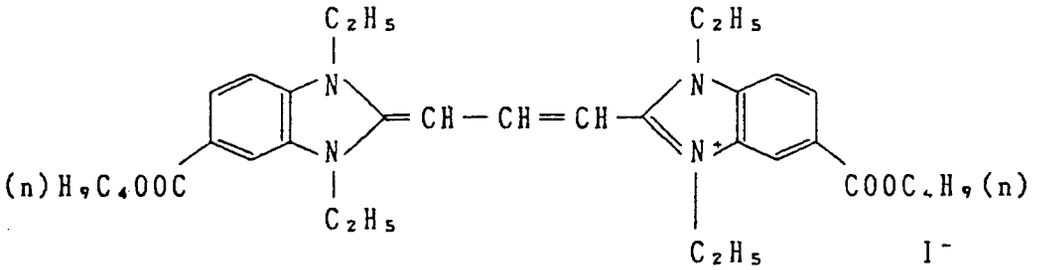

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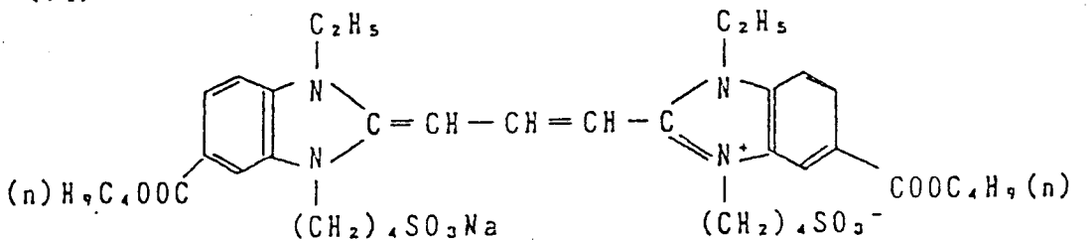

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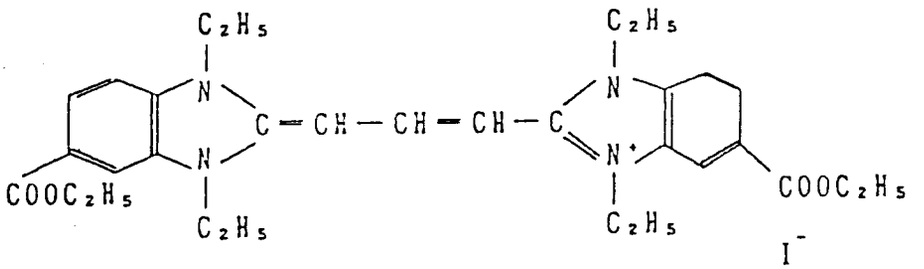

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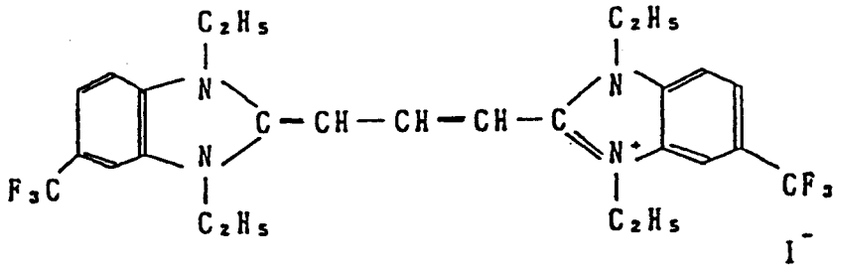
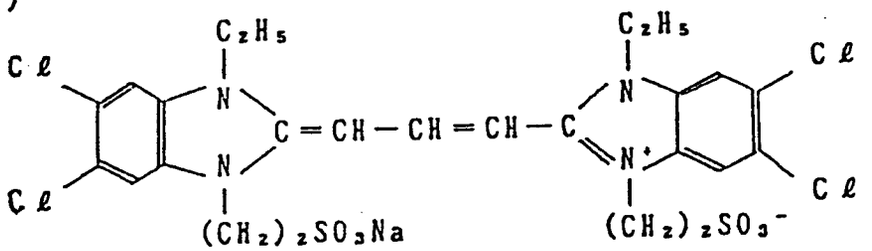


(77)



The compounds of formulae (I), (II) and (III) may be used, for example, in an amount of from 10 mg to 900 mg in total per 1 mole of silver halide. The amount is preferably from 60 mg to 600 mg.

The compounds of formulae (I), (II) and (III) may be added at any position in the course of the production of the light-sensitive materials. For example, they may be added anywhere before chemical ripening, during chemical ripening, after termination of chemical ripening or before coating.

The light-sensitive material of this invention is suitable for high speed processing, and excellent photographs can be obtained without the problems mentioned above even when used, for example, in ultra rapid processing as mentioned above.

The light-sensitive material of this invention is preferably processed in an automatic processor having a processing time of from 20 to 60 seconds.

A preferred embodiment is to use a silver halide photographic emulsion comprising silver halide grains substantially comprising silver iodobromide and having a multi-layer structure, the difference in average iodide content between any two layers having uniform iodine distribution (between coats or between an inner nucleus and a coat) adjacent to each other in the multi-layers of the silver halide grains being 10 mole % or less.

It is further preferred that the outermost layer has an average iodide content of 10 mole % or less, and that the silver halide grains are chemically sensitized.

The grains having a multi-layer structure have an inner nucleus with a coat that may have any halogen composition. This coat may comprise only one layer or may be laminated to form two or more layers, for example, three layers or four layers, but preferably not more than five layers.

As silver halides for use in the inner nucleus and the coats, silver bromide, silver iodobromide and silver iodide are used; they may be in a mixture with a small amount of silver chloride. Specifically, the mixture may contain 10 mole % or less, preferably 5 mole % or less, silver chloride.

The outermost layer preferably comprises substantially silver bromide or substantially silver iodobromide (iodide content: 10 % or less), and may contain less than several percent chloride.

The average total iodide content in the silver halide grains is preferably 10 mole % or less, more preferably 6 mole % or less.

In, for example, X-ray light-sensitive materials, iodide may sometimes aggravate problems such as development inhibition and infectious development, and therefore it is preferred to use an iodide content of not more than a certain level. This invention is effective for decreasing fogging by pressure, and, for such a reason, the total iodide content in all of the grains is preferably 10 mole % or less, more preferably 7 mole % or less, and most preferably 5 mole % or less.

When the inner nucleus comprises silver iodobromide, it is preferably a homogeneous phase of a solid solution.

Here, "homogeneous" is more specifically explained as follows:

When an analysis by X-ray diffraction is effected on the silver halide grain powder, the half-width at a

peak of area index [200] of silver iodide with Cu-K_β X-rays is $\Delta 2\theta$ = 0.30 (deg) or less. The conditions under which a diffractometer is used is such that $\omega\tau/r \leqq 10$, assuming the scanning speed of a goniometer is ω(deg/min), the time constant is τ(s) and the receiving slit width is r(mm).

The halide composition of the inner nucleus is such that the average iodide content is preferably 40 mole % or less, more preferably from 0 to 20 mole %.

The difference in the silver iodide content between two layers adjacent to each other (any two coats, or a coat and an inner nucleus) is preferably not less than 10 mole 96, more preferably not less than 20 mole 96, and particularly preferably not less than 25 mole %.

The silver iodide content in a coat other than the outermost coat is preferably from 10 mole % to 100 mole %.

When the silver halide grains comprise 3 or more layers and the coats comprise silver iodobromide, they may not necessarily be all homogeneous, but it is preferred for all layers to comprise homogeneous silver iodobromide.

Such coats (or inner nucleus) having a high iodide content are preferably present below the outermost layer in the case of a negative type silver halide emulsion. In the case of a positive type silver halide emulsion, they may be present either in the inside or at the surface.

The silver iodide content in the outermost coat is preferably not more than 10 mole %, more preferably from 0 to 5 mole %.

The iodide content in the inner nucleus and the coats of the silver halide grains can also be determined by the method disclosed in J.I. Goldstein and D.B. Williams, "X-ray Analysis in TEM/ATEM", Scanning Electron Microscopy (1977), Vol. 1, (I.I.T. Research Institute), p.651 (March, 1977).

When the silver halide grains comprise, for example, two layers, the inner nucleus preferably has a higher iodide content than the outermost layer, and, when it comprises three layers, the coats other than the outermost layer or the inner nucleus preferably have a higher iodide content than the outermost layer.

This invention is preferably applied in respect of silver halide grains which have been chemically sensitized. This is because unsensitized grains may have very poor sensitivity, and neither abrasion blackening nor pressure desensitization may occur in the first place.

The silver halide grains may be of positive type or of negative type.

In the case of negative type, chemical sensitization is preferably carried out to such a degree that it gives 60 % or more of the optimum sensitization degree when taking a sensitivity point of "fog + 0.1" in the optical density.

In the case of positive type, chemical sensitization is preferably applied to the inside of grains to such a degree that it gives 60 % or more of the optimum sensitization degree when taking a sensitivity point of "fog - 0.1" in the optical density.

Further silver halide grains which can be used are a combination of internal fog type silver halide grains with surface latent image type silver halide grains as disclosed in Japanese Patent Publication No. 2068/1966.

The average grain size of the silver halide grains is expressed as the edge length of a grain having a volume equal to the average volume of the grains.

In a preferred embodiment of the invention the silver halide emulsion grains used in the silver halide emulsion layers have an average grain size of 0.30 to 1.50 μm, more preferably 0.40 to 1.30 μm, and most preferably 0.40 to 1.10 μm.

The grain size distribution may be either narrow or wide.

The silver halide grains contained in the photographic emulsion may have any grain size distribution, but may particularly be monodispersed. The term "monodispersed" means a system wherein 95 % of the grains are included in ± 60 %, preferably in ± 40 %, of the number average grain size. The number average grain size refers to the number average diameter of the projected area of the silver halide grains.

The silver halide grains in the photographic emulsion may have a regular crystal form such as a cube, an octahedron, a tetradecahedron or a dodecahedron, an irregular crystal, form such as a sphere or a plate, or a composite form of these crystal forms. The grains may comprise grains of various crystal forms.

Also available are, for example, junction type silver halide crystals formed by combining crystals of oxides such as PbO with crystals of silver halides such as silver chloride, silver halide crystals formed by epitaxial growth (for example, silver chloride, silver iodobromide or silver iodide epitaxially grown on silver bromide), hexagonal crystals and crystals formed by epitaxy of regular hexahedral silver chloride on regular octahedral silver iodide.

An emulsion comprising silver halide grains comprising an ultra flat plate having diameter of 5 times or more of its thickness accounting for 50 % or more of total projection area may also be used. Details are disclosed in, for example, Japanese Unexamined Patent Publications No. 127921/1983 and No.

113927/1983.

The regular grains mentioned above refer to a silver halide emulsion wherein at least 80 % by weight or number of the grains have a regular form. Silver halide grains which are regular in structure or form also include grains which have been isotropically grown without any anisotropic growth of, for example, twin crystal faces, and which have the shape of, for example, a cube, a tetradecahedron, a regular octahedron, a dodecahedron or a sphere. A method for the production of such regular silver halide grains is disclosed in, for example, Journal of Photographic Science, 5, 332 (1961), Berchte der Bunsenges Physik Chemi, 67, 949 (1963) and International Congress of Photographic Science of Tokyo (1967). Such regular silver halide grains can be obtained by controlling the reaction conditions when allowing silver halide grains to grow using a simultaneous mixing method. In such a simultaneous mixing method, silver halide grains can be obtained by adding to an aqueous solution of a protective colloid, a silver nitrate solution and a halide solution in substantially equimolar amounts with vigorous stirring.

In working this invention, when incorporating, for example, the regular silver halide grains mentioned above, it is also possible to incorporate irregular silver halide grains. However, when such grains are present, it is generally better for them not to be included in an amount of 50 % or more by weight or number. In a preferred embodiment, an emulsion comprises at least 60 to 70 % by weight of regular silver halide grains.

When producing the monodispersed emulsion and/or the emulsion having regular silver halide grains, the silver ions and halide ions are preferably fed by gradually increasing, in a continuous or stepwise manner, the growth rate at a critical growth rate, or within a suitable tolerance thereof, for feeding the silver halide necessary and sufficient for the growth of existing grains only, without dissolving the existing crystal grains, and without the generation or growth of new grains, accompanying the growth of the crystal grains. This method is disclosed in Japanese Patent Publications No. 36890/1973 and No. 16364/1977 and Japanese Unexamined Patent Publication No. 142329/1980.

In other words, silver ions and halide ions are effectively fed at such a rate that the rate of growth of silver halide grains is from 30 to 100 % of the critical growth rate.

This critical growth rate varies depending on, for example, the temperature, the pH, the pAg, the degree of stirring, the composition of the silver halide grains, the solubility, the grain size, the distance between grains, the crystal form and the nature and density of the protective colloid. It can readily be determined by experiment, for example by microscopic observation of emulsion grains suspended in a liquid phase or by measurement of turbidity.

The silver halide grains used in the silver halide emulsion can be produced by, for example, a neutral method, an acidic method, an ammonia method, a regular mixing method, a reverse mixing method, a double jet method, a controlled double jet method, a conversion method or a core/shell method, as disclosed in, for example, T.H. James, The Theory of the Photographic Process, 4th Ed., published by Macmillan Publishing Co., Inc. (1977); P. Glfkides, Chemie et Physique Photographigue, published by Paul Montel Co., 1967; G.F. Duffin, Photographic Emulsion Chemistry, published by The Focal Press, 1966; and V.L. Zelikman et al, Making and Coating Photographic Emulsion, published by The Forcal Press, 1964.

As an alternative to the double jet method, a triple jet method can be used, in which soluble halogen salts having different compositions (for example, a soluble silver salt, a soluble bromine salt and a soluble iodine salt) are each independently added.

It is also possible to use a method in which grains are formed in the presence of excess silver ions (the so-called reverse mixing method). As one embodiment of the simultaneous mixing method, it is possible to keep the pAg constant in the liquid phase in which the silver halide is formed. This is the so-called controlled double jet method.

According to this method, it is possible to obtain a silver halide emulsion having a regular crystal form and substantially uniform grain size.

In forming silver halide grains, a silver halide solvent, for example, ammonia, potassium thiocyanate, ammonium thiocyanate, thioether compounds (see, for example, U.S. Patents No. 3,271,157, No. 3,574,628, No. 3,704,130, No. 4,297,439 and No. 4,276,374), thion compounds (see, for example, Japanese Unexamined Patent Publications No. 144319/1978, No. 82408/1978 and No. 77737/1980) and amine compounds (see, for example, Japanese Unexamined Patent Publication No. 100717/1979) can be used to control the growth of grains. Among them, ammonia is preferred.

Two or more kinds of silver halide emulsions separately produced may be also used by mixing them together.

These silver halide grains or the silver halide emulsion preferably contain at least one soluble salt of iridium, thallium, palladium, rhodium, zinc, nickel, cobalt, uranium thorium, strontium, tungsten or platinum. The salt is preferably contained in an amount of from 10^{-6} to 10^{-1} mole per mole of silver. At least one salt

of thallium, palladium or iridium is preferred. These may be used alone or in combination, and any position (or time) of addition may be selected. There can be expected effects such as an improvement in, for example, flash exposure performance, prevention of pressure desensitization, prevention of latent image fading and sensitization.

A mother liquor containing protective colloids is preferably kept such that the pAg is at least 10.5 or more during the course of the grain growth effected before the chemical sensitization mentioned above. Particularly preferably, the grains should be allowed to pass at least once through an environment of pAg 11.5 or more containing a great excess of bromide ions. In this manner, the (111) face is increased and the grains are rounded, whereby the effect of this invention can be increased. Such a (111) face preferably accounts for 5 % or more of the total surface area of the grains.

In such a case, the rate of increase in the (111) face (the rate of increase relative to the grain having not yet been allowed to pass through the environment of pAg 10.5 or more) is preferably not less than 10 %, more preferable from 10 to 20 %.

As to which of the (111) face or (100) face covers the outer surface of a silver halide grain, or how to measure the ratio therebetween, there is a disclosure by Akira Hirata in "Bulletin of the Society of Scientific Photography of Japan", No. 13, pp.5-15 (1963).

In the course of the grain growth effected before chemical sensitization, grains may be allowed to pass once through an environment where a mother liquor containing protective colloids is kept at a pAg of at least 10.5, whereby it can be readily confirmed by Hirata's measurement method whether the (111) face is increased to 5 % or more.

In this case, the mother liquor may be made to have the above pAg preferably at the time after having added about 2/3 of the total amount of silver and before a desalting step which is generally carried out before chemical sensitization. This is because a monodispersed emulsion having a wide grain size distribution can thus be readily obtained.

The ripening in the environment of pAg 10.5 or more is preferably effected for 2 minutes or more.

By controlling the pAg in this manner, the (111) face can be increased to 5 % or more and the grain can have a roundish shape. Thus a preferred grain having 5 % or more of the (111) face, relative to the total surface area of the grain, can be obtained.

In order to remove soluble salts from an emulsion after the formation of precipitates or after physical ripening, a noodle washing method which is carried out by gelation of gelatin may be used, or a sedimentation method (or a floculation method) utilizing inorganic salts, anionic surface active agents, anionic polymers (for example, polystyrene sulfonic acid) or gelatin derivatives (for example, acylated gelatin or carbamoylated gelatin) may also be used. The step of removing soluble salts may be omitted.

The silver halide emulsion may or may not be chemically sensitized, but is preferably chemically sensitized. The method disclosed in H. Frieser, Die Grundlagen der Photo-graphischen Prozesse mit Silberhalogeniden, Akademische Verlagaesellschaft, 1968, pp.675-734 can, for example, be employed.

More specifically, there can be employed alone or in combination a sulfur sensitization method using an active gelatin or a sulfur-containing compound capable of reacting with silver (for example, thiosulfate, thioureas, mercapto compounds or rhodanines); a reduction sensitization method using a reducible substance (for example, a silver-tin salt, amines, hydrazine derivatives, formamidinesulfinic acid or silane compounds); and a noble metal sensitization method using a noble metal compound (for example, gold complex salts, as well as complex salts of Group VIII metals in the periodic table such as Pt, Ir or Pd).

Specific examples are disclosed in U.S. Patents No. 1,574,944, No. 3,410,689, No. 2,278,947, No. 2,728,668 and No. 3,656,955 in respect of the sulfur sensitization method; U.S. Patents No. 2,983,609, No. 2,419,974 and No. 4,054,458 in respect of the reduction sensitization method; and U.S. Patents No. 2,599,083 and No. 2,448,060 and British Patent No. 618,061 in respect of the noble metal sensitization method.

The photographic emulsion may be spectrally sensitized, for example by a methine dye. The dye usable includes cyanine dyes, merocyanine dyes, composite cyanine dyes, composite merocyanine dyes, holopolarcyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly useful dyes are cyanine dyes, merocyanine dyes and composite merocyanine dyes. In these dyes, any nuclei usually utilized in cyanine dyes as a basic heterocyclic ring nuclei can be used. There can be used, for example, a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrol nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus or a pyridine nucleus; a nucleus wherein an aliphatic hydrocarbon nucleus is fused with any of the above nuclei; and a nucleus wherein an aromatic hydrocarbon is fused with any of the above nuclei, for example an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus or a

quinoline nucleus. These nuclei may be substituted on a carbon atom.

In the merocyanine dyes or the composite merocyanine dyes, a 5- or 6-membered heterocyclic ring nuclei such as a pyrazolin-5-on nucleus, a thiohydantoin nucleus, a 2-thiooxazolidine-2,4-dion nucleus, a thiazolidine-2,4-dion nucleus, a rhodanine nucleus or a thiobarbituric acid nucleus can be used as a nuclei having a ketomethylene structure.

Specific examples of spectral sensitizing dyes are disclosed in P. Glafkides, "Chemie Photographigue", 2nd Ed., 1957; Paul Montel, Paris, Articles 35 to 41; F.M. Hamer, "The Cyanine and Related Compounds", Interscience; and U.S. Patents No. 2,503,776, No. 3,459,553 and No. 3,117,210 and Research Disclosure Vol. 176, 17643, published December, 1978, Paragraph 23-IV-J.

Sensitizing dyes may be used alone or may be used in combination. A combination of sensitizing dyes is frequently used, particularly for supersensitization.

Typical examples are disclosed in U.S. Patents No. 2,688,543, No. 2,977,229, No. 3,397,060, No. 3,322,052, No. 3,327,601, No. 3,617,293, No. 3,636,960, No. 3,666,450, No. 3,272,898, No. 3,679,428, No. 3,703,377, No. 3,769,301, No. 3,814,609, No. 3,537,562 and No. 4,026,707, British Patents No. 1,344,281 and No. 1,207,503, Japanese Patent Publications No. 4536/1970 and No. 12373/1978 and Japanese Unexamined Patent Publications No.110615/1978 and No. 109923/1978.

The sensitizing dye can be used in a concentration which is the same as that used in ordinary negative type silver halide emulsions. It is particularly advantageously used in a concentration that does not substantially lower the sensitivity inherent in a silver halide emulsion. The sensitizing dye is preferably used in a concentration of from 1.0×10^{-5} to 5.0×10^{-4} mole per mole of silver halide, particularly from 4.0×10^{-5} to 2.0×10^{-4} mole per mole of silver halide.

Together with the sensitizing dye, the emulsion may contain a dye having itself no spectral sensitization action, or a substance substantially absorbing no visible light and having supersensitization.

For example, it may contain an aminostilbene compound (for example, the compounds disclosed in U.S. Patents No. 3,533,590 and No. 3,638,721), an aromatic organic acid/formaldehyde condensate (for example, the compounds disclosed in U.S. Patent No. 3,743,510), a cadmium salt or an azaindene compound. Particularly effective are the combinations disclosed in U.S. Patents No. 3,615,615, No. 3,615,641, No. 3,617,295 and No. 3,635,921.

The photographic emulsion may contain various compounds to prevent togging during production, storage or photographic processing of the light-sensitive materials, or to make the photographic performance stable. That is, there can be added a variety of compounds known as antifoggants or stabilizers, including thiazoles, for example, benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazsoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles and mercaptotetrazoles (in particular, 1-phenyl-5-mercaptotetrazole); mercaptopyrimidines; mercaptotriazines; thioketo compounds such as oxazoline thion; azaindenes, for example, triazaindenes, tetrazaindenes (in particular, 4-hydroxy substituted (1,3,3a,7)tetrazaindenes) or pentazaindenes; benzenethiosulfonic acid, benzenesulfinic acid or benzenesulfonic acid amide.

Details are available in, for example, E.J. Birr, "Stabilization of Photographic Silver Halide Emulsions", Focal Press, 1974.

Usable compounds include, for example, thiazolium salts disclosed in U.S. Patents No. 2,131,038 and No. 2,694,716; azaindenes disclosed in U.S. Patents No. 2,886,437 and No. 2,444,605; urazoles disclosed in U.S. Patent No. 3,287,135; sulfocatechols disclosed in U.S. Patent No. 3,236,632; oxymes disclosed in British Patent No. 623,448; mercaptotetrazoles disclosed in U.S. Patents No. 2,403,927, No. 3,266,897 and No. 3,397,987; nitron; nitroindazoles; polyvalent metal salts disclosed in U.S. Patent No. 2,839,403; thiuronium salts disclosed in U.S. Patent No. 3,220,839; and salts of palladium, platinum or gold disclosed in U.S. Patents No. 2,566,263 and No. 2,597,715.

The light-sensitive material of this invention may contain a water soluble dye as a filter dye or to prevent irradiation and halation, or for any other purpose. Such a dye includes oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes and azo dyes. Among them, oxonol dyes, hemioxonol dyes and merocyanine dyes are particularly useful.

In the light-sensitive material of this invention, when a dye or an ultraviolet absorbent is contained in a hydrophilic colloid layer, it may be mordanted, for example by a cationic polymer.

Such a dye includes the compounds disclosed in Absorbing and Filter Dyes in Research Disclosure Vol. 176, pp.23-26.

To increase sensitivity, increase contrast or accelerate development, the photographic emulsion layers of the light-sensitive photographic material of this invention may contain, for example, polyalkylene oxides, derivatives thereof such as an ether, ester and amine thereof, thioether compounds, thiomorpholines,

quaternary ammonium chloride compounds, urethane derivatives, urea derivatives, imidazole derivatives or 3-pyrazolidones.

It is advantageous to use gelatin as a binding material or a protective colloid in emulsion layers or intermediate layers of the light-sensitive material of this invention. However, it is also possible to use another hydrophilic colloid alone or in combination with gelatin.

When gelatin is used in working this invention, the gelatin may, for example, be either lime-treated or treated with an acid. Details of a method for producing gelatin are disclosed in Arther Davis, The Macromolecular Chemistry of Gelatin, Academic Press(published 1964).

The hydrophilic colloid includes, for example, proteins such as gelatin derivatives, graft polymers of gelatin with other macromolecules, albumin and casein; cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose and cellulose sulfuric acid esters; sugar derivatives such as sodium alginate and starch derivatives; and various synthetic hydrophilic macromolecular substances such as homopolymers or copolymers of polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinyl pyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole or polyvinyl pyrazole.

In the light-sensitive photographic material of this invention, the photographic emulsion layers and other hydrophilic colloid layers may contain an inorganic or organic hardening agent. For example, there can be used, alone or in combination, chromium salts (such as chrome alum and chromium acetate), aldehydes (such as formaldehyde, glyoxal and glutalaldehyde), N-methylol compounds (such as dimethylol urea and methyloldimethylhydantoin), dioxane derivatives (such as 2,3-dihydroxydioxane), active vinyl compounds (such as 1,3,5-triacryloyl-hexahydro-2-triazine and 1,3-vinylsulfonyl-2-propanol), active halogen compounds (such as 2,4-dichloro-6-hydroxy-3-triazine) or mucohalogen acids (such as mucochloric acid and mucophenoxychloric acid).

In the light-sensitive photographic material of this invention, the photographic emulsion layers and other hydrophilic colloid layers may contain a dispersed product of a water soluble or slightly soluble synthetic polymer to improve the dimensional stability. For example, there can be used, solely or in combination, alkyl acrylates or methacrylates, alkoxyalkyl acrylates or methacrylates, glycidyl acrylates or methacrylates, acryl-or methacrylamide, vinyl esters (for example, vinyl acetate), acrylonitriles, olefins, styrenes or polymers having monomer components comprising a combination of these with, for example, acrylic acid, methacrylic acid, α,β-unsaturated dicarboxylic acid, hydroxyalkyl acrylates or methacrylates, sulfoalkyl acrylates or methacrylates or styrenesulfonic acid.

A protective layer is preferably used in the light-sensitive silver halide photographic material of this invention. The protective layer is a layer comprising a hydrophilic colloid, and, as the hydrophilic colloid, there can be used those mentioned before. The protective layer may comprise either a single layer or overlapped layers.

A matte agent and/or a smoothing agent may, for example, be added to the emulsion layers or the protective layer, preferably to the protective layer, of the light-sensitive silver halide photographic material of this invention. Examples of the matte agent preferably used include organic compounds such as water dispersible vinyl polymers including polymethyl methacrylate having a suitable grain size (preferably a grain size of from 0.3 to 5 μm, or twice or more, particularly four times or more, of the thickness of the protective layer), or inorganic compounds such as silver halide and strontium or barium sulfate. The smoothing agent is useful to prevent adhesion trouble similarly to the matte agent, and also to improve the friction characteristics having a relation to the adaptability to cameras when taking photographs of motion picture films or projecting motion pictures. Specific examples that can be preferably used include waxes such as liquid paraffin and higher aliphatic acid esters; polyfluorinated hydrocarbons or derivatives thereof; and silicones such as polyalkyl polysiloxane, polyaryl polysiloxane, polyalkylaryl polysiloxane or alkylene oxide addition derivatives of these.

If necessary, other additives can be used in the light-sensitive photographic material of this invention. For example, they may include a dye, a development accelerator, a brightening agent, a color fog preventive agent or an ultraviolet absorbent. Specifically, there can be used those disclosed in Research Disclosure No. 176, pp.22-31 (RD-17643, 1978).

In addition, if necessary, the light-sensitive silver halide photographic material of this invention can be provided with, for example an antihalation layer, an intermediate layer or a filter layer.

In the light-sensitive photographic material of this invention, the photographic emulsion layers or other layers are applied to one or both sides of a flexible support usually used in light-sensitive materials. Useful flexible supports are, for example, films comprising semisynthesized or synthesized macromolecules such as cellulose nitrate, cellulose acetate, cellulose acetate butylate, polystyrene, polyvinyl chloride, polyethylene terephthalate or polycarbonate; and paper coated or laminated with a baryta layer or an α-olefin polymer (for example, polyethylene, polypropylene or an ethylene/butene copolymer). The support may be

colored by a dye or pigment. It may be made black for light interception. The surfaces of these supports are, in general, subbing-treated to improve the adhesion of a photographic emulsion. The surface of the support may be submitted to, for example, corona discharge ultraviolet irradiation or flame treatment before or after the subbing treatment. Those disclosed in the paragraph "Supports" in Research Disclosure, Vol. 176, p.25 may be used.

In the light-sensitive photographic material of this invention, the photographic emulsion layers or other hydrophilic colloid layers can be applied to a support or other layers by various coating methods. Examples of coating methods are a dip coating method, a roller coating method, a curtain coating method and an extrusion coating method. The method disclosed in the paragraph "Coating Procedures" in Research Disclosure, Vol. 176, pp.27-28 may be used.

The light-sensitive silver halide photographic material of this invention can, for example, be used specifically as an X-ray light-sensitive material, lithographic light-sensitive material, black and white photography light-sensitive material, color negative light-sensitive material, color reversal light-sensitive material, color photographic paper, colloid transfer process material, silver salt diffusion transfer process material, dye transfer process material, silver dye bleaching method material, print-out sensitive material or heat development sensitive material.

The exposure for obtaining a photographic image may be carried out by conventional methods. Namely, there can be used any light source containing ultraviolet light, including natural light (sunlight), a tungsten lamp, a fluorescent lamp, a mercury lamp, a xenon arc lamp, a carbon arc lamp, a xenon flash lamp, a cathode ray tube flying spot, a light-emitting diode or laser beams (for example from a gas laser, a YAG laser, a dye laser or a semiconductor laser). Exposure may also be carried out by light emitted from phosphors excited by, for example, electron rays, X-rays, gamma rays or alpha rays. Exposure may be carried out for 1/1000 second to 1 second as in ordinary cameras, as well as for a time shorter than 1/1000 second, for example, from $1/10^4$ to $1/10^6$ second using a xenon flash lamp or a cathode ray tube, or for longer than 1 second. If necessary, the spectral composition of light used in exposure can be controlled using a color filter.

Any of the methods and processing solutions disclosed in, for example, Research Disclosure No. 176, pp.25-30 (RD-17643) can be used for the photographic processing of the light-sensitive material of this invention. This photographic processing may be either photographic processing for the formation of silver images (i.e. black and white photographic processing) or photographic processing for the formation of color images (i.e. color photographic processing). The processing temperature is usually from 18 °C to 50 °C, but may be lower than 18 °C or higher than 50 °C.

Other development methods (for example heat development) can be used as occasion demands.

A developing solution used when, for example, carrying out black and white processing may contain known developing agents. There can, for example, be used as the developing agents, solely or in combination, dihydroxybenzenes (for example, hydroquinone), 3-pyrazolidones (for example, 1-phenyl-3-pyrazolidone) or aminophenols (for example, N-methyl-n-aminophenol). In general, besides these, the developing solution may, for example, contain a preservative, an alkali agent, a pH buffering agent or an antifoggant, and may, for example, further contain, if necessary, a dissolution auxiliary, a color toning agent, a development accelerator, a surface active agent, an antifoaming agent, a hard water-softening agent, a hardening agent or a viscosity-imparting agent.

As a special developing processing system, there may be employed a method in which a development agent is incorporated in a light-sensitive material, for example, in emulsion layers, and the light-sensitive material is developed in an aqueous alkali solution. As the development agent, a hydrophobic development agent can be incorporated in the emulsion layers according to the methods disclosed in Research Disclosure No. 169 (RD-16928), U.S. Patent No. 2,739,890, British Patent No. 813,253 and West German Patent No. 15 47 763. Such a developing processing may be combined with a silver salt stabilizing processing carried out using a thiocyanate.

As a fixing solution, that having a formulation as generally employed can be used. As a fixing agent, there can be used thiosulfate and thiocyanate, as well as organic sulfur compounds known to be effective as fixing agents. The fixing solution may contain a water soluble aluminum salt as a hardening agent.

The photographic emulsion layer of the light-sensitive photographic material of the present invention may contain a color image-forming coupler, i.e. a compound capable of forming a dye by reacting with an oxidized product of an aromatic primary amine (for example a phenylenediamine derivative or aminophenol derivative) developing agent in color developing processing. For example, as a magenta coupler, there may be included 5-pyrazolone couplers, pyrazolobenzimidazole couplers, cyanoacetylcumarone couplers and open chain acylacetonitrile couplers; as a yellow coupler, acylacetamide couplers (for example, benzoylacetanilides and pivaloylacetanirides); and as a cyan coupler, a naphthol coupler and a phenol coupler.

These couplers are preferably non-diffusible couplers having a hydrophobic group called a ballast group in the molecules. The couplers may be either of the four equivalent type or two equivalent type relative to the silver ions. There may be also included colored couplers having a color correcting effect or couplers capable of releasing a development restrainer as the development proceeds (the so-called DIR couplers).

Besides the DIR couplers, there may be included colorless DIR coupling compounds that form a colorless product by the coupling reaction and release a development restrainer.

The light-sensitive silver halide photographic material of this invention may contain a color fog preventive agent, for example hydroquinone derivatives aminophenol derivatives, gallic acid derivatives or ascorbic acid derivatives.

The light-sensitive silver halide photographic material of this invention may contain an ultraviolet absorbent in the hydrophilic colloid layer. For example, there can be used benzotriazole compounds substituted with an aryl group (for example, those disclosed in U.S. Patent No. 3,533,794), 4-thiazolidone compounds (for example, those disclosed in U.S. Patents No. 3,314,794 and No. 3,352,651), benzophenone compounds (for example, those disclosed in Japanese Unexamined Patent Publication No. 2784/1971), cinnamic acid ester compounds (for example, those disclosed in U.S. Patents No. 3,705,805 and No. 3,705,375), butadiene compounds (for example, those disclosed in U.S. Patent No. 4,045,229), or benzooxydole compounds (for example, those disclosed in U.S. Patent No. 3,700,455). Those disclosed in U.S. Patent No. 3,499,762 and Japanese Unexamined Patent Publication No. 48534/1979 can be further used. Couplers having ultraviolet absorbing properties (for example, cyan dye-forming couplers of the α-naphthol type) or polymers having ultraviolet absorbing properties may be also used. These ultraviolet absorbents may be mordanted in a particular layer.

A variety of anti-color-fading agents as shown below can be used in combination, and color image stabilizers used in this invention can be used alone or in combination of two or more of them. The anti-color-fading agents include hydroquinone derivatives, gallic acid derivatives, p-alkoxyphenols, p-oxyphenol derivative and bisphenols.

In general, a color developing solution may comprise an alkaline aqueous solution containing a color development agent. The color developing agent that can be used includes various primary aromatic amine developing agents such as phenylenediamines (for example, 4-amino-N,N-diethylamine, 3-methyl-4-amino-N,N-diethylaniline, 4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfoamide ethylaniline or 4-amino-3-methyl-N-ethyl-N-β-methoxyethylaniline).

Besides these, those disclosed in, for example, L.F.A. Mason, Photographic Processing Chemistry, Focal Press (1966), pp.226-229, U.S. Patents No. 2,193,015 and No. 2,592,364 and Japanese Unexamined Patent Publication No. 64933/1973, may also be used.

The color developing solution may further contain, for example, a pH buffering agent such as an alkali metal sulfite, carbonate, borate or phosphate or a development restrainer or antifoggant such as a bromide, iodide or organic antifoggant. If necessary, it may also, for example, contain a hard water softening agent, a preservative such as hydroxylamine, an organic solvent such as benzyl alcohol and diethylene glycol, a development accelerator such as polyethylene glycol, quaternary ammonium salts and amines, a color dye-forming coupler, a competing coupler, a fogging agent such as sodium boron hydride, an auxiliary developing agent such as 1-phenyl-3-pyrazolidone, a viscosity imparting agent, a polycarboxylic acid type chelating agent or an antioxidant.

After the color development, the photographic emulsion layers are usually subjected to a bleaching processing. The bleaching processing may be carried out simultaneously with a fixing processing, or may be carried out separately. As a bleaching agent, there may be used, for example, polyvalent metal compounds such as those of iron (III), cobalt (III), chrome (VI) and copper (II), peracids, quinones or nitroso compounds.

For example, there can be used ferricyanide, dichromate, organic complex salts of iron (III) or cobalt (III), for example, complex salts of aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, nitrilotriacetic acid and 1,3-diamino-2-propanoltetraacetic acid, or of organic acids such as citric acid, tartaric acid and malic acid; persulfate; permanganate; or nitrosophenol. Of these, particularly useful are potassium ferricyanide, sodium ethylenediaminetetraacetic acid iron (III) and ammonium ethylenediaminetetraacetic acid iron (III). Ethylenediaminetetraacetic acid iron (III) complex salts are useful in both an independent bleaching solution and a combined bleach fixing solution.

This invention is now further described in the following Examples.

Example 1

A silver iodobromide emulsion E-1 containing 2.0 mole % of silver iodide was first prepared by regular mixing in a full ammonia method. This emulsion comprised grains having an average grain size of 1.10 μm. This silver iodobromide emulsion E-1 was subjected to an optimum gold/sulfur sensitization by adding chloroauric acid, sodium thiosulfate and ammonium thiocyanate, and stabilized with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene.

Both sides of a polyester film support having been subjected to a subbing treatment were coated with the above stabilized emulsion and a protective layer to which a hardening agent was added, to provide layers in the order of the silver halide emulsion layer and the protective layer according to a slide hopper method at a coating rate of 100 m/min so that two layers simultaneously overlap, thereby obtaining Samples No. 1 to No. 28 shown in Table 1 (Table 1-a, -b, -c). The coated silver weight was 55 mg/dm^2.

The amount of hardening agent in each of the above samples was controlled such that the melting time was about 25 minutes. The melting time is the time by which an emulsion layer begins to melt out after a sample (a light-sensitive silver halide photographic material) cut into 1 cm x 2 cm was dipped in an aqueous solution of 1.5 % sodium hydroxide at 50 ° C.

Subsequently, the number and extent of coating troubles (such as coating streaks and coating uneveness) in the samples were measured and indicated by a five rank system ranging from 1 (poor) to 5 (excellent). There is no problem when it is 3 to 5, but a rank of 1 to 2 means infeasibleness for practical use.

The sensitivity was also measured as follows. A sample was interposed between two optical wedges wherein the density inclination was mirror-symmetrically adjusted, and exposed in an equal amount from both sides for 1/12.5 second with a light source having a color temperature of 5,400 K.

Processing was carried out according to the following steps using an automatic processor of a roller conveyor type. The total processing time was 45 seconds.

	Processing temperature	Processing time
Insertion	-	1.2 s
Developing & passing	35 ° C	14.6 s
Fixing & passing	33 ° C	8.2 s
Washing & passing	25 ° C	7.2 s
Squeegeeing	40 ° C	5.7 s
Drying	45 ° C	8.1 s
Total	-	45.0 s

The developing solution and fixing solution used were XD-90 and XF, respectively (both trade names; produced by Konishiroku Photo Industry Co., Ltd.).

Based on the characteristic curve showing the relationship between log E (the logarithm of the exposure amount) and D (optical density), the exposure amount at base density + fog density + 1.0 was obtained to determine the relative sensitivity.

The drying characteristics were also evaluated as follows. After carrying out the above automatic processing, a touch on the samples having passed through the drying area and the degree of sticking to other samples were overall evaluated by the 5 rank system ranging from 1 (poor) to 5 (excellent). There is no problem when it is 3 to 5, but a rank of 1 to 2 means infeasibleness for practical use. The results obtained are shown together in Table 1 (Table 1-c). At the far right column of the table, a sample according to this invention is indicated as "Yes", and a sample not according thereto as "No".

Part of the samples were processed to obtain the sensitivity in a conventional 90 second processing by dropping the line speed of the above 45 second automatic processor to one half. The results obtained are shown in Table 2.

As is clear from Table 1 (Table 1-a, -b, -c) and Table 2, the samples (light-sensitive silver halide photographic materials) of this invention have good coating properties and also have excellent sensitivity and drying characteristics, and thus are suitable for ultra rapid processing. It is also seen from the comparison with the conventional 90 second processing that the processing time can be shortened to 1/2 to provide twice the processing ability, retaining the sensitivity attained in the conventional system.

Table 1:

(Table 1-a)

Sample No.	Silver halide emulsion layer			
	Gelatin amount per one side (g/m^2)	Surface active agent		Surface tension (dyn/cm) (mN/m)
		Type	Amount per one side (g/m^2)	
1	2.20	1-10	1×10^{-3}	36
2	"	"	"	36
3	"	"	"	36
4	2.00	"	"	"
5	"	"	"	"
6	"	"	"	"
7	1.90	"	1.5×10^{-3}	"
8	"	"	"	"
9	"	"	"	"
10	"	"	"	"
11	1.75	"	2×10^{-3}	35
12	"	"	"	"
13	"	"	"	"
14	"	"	"	"
15	"	"	"	"
16	1.70	"	"	35
17	"	"	"	"
18	"	"	"	"
19	"	"	"	"
20	"	"	"	"
21	1.20	"	4×10^{-3}	34
22	"	"	"	"
23	"	"	"	"
24	"	"	"	"
25	"	"	"	"
26	1.10	"	"	34
27	"	"	"	"
28	"	"	"	"

(Table 1-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Protective layer: Surface active agent: Type	Protective layer: Surface active agent: Amount per one side (g/m^2)	Surface tension (dyn/cm) (mN/m)
1	1.15	1-10	5×10^{-4}	31
2	1.15	"	8×10^{-4}	30
3	1.15	"	1×10^{-3}	28
4	1.15	3-3	4×10^{-4}	31
5	"	"	7×10^{-4}	30
6	"	"	1.3×10^{-3}	28
7	"	2-70	4×10^{-4}	31
8	"	"	7×10^{-4}	30
9	"	"	1×10^{-3}	28
10	"	"	4×10^{-3}	26
11	"	2-6	7×10^{-4}	30
12	"	"	1×10^{-3}	29
13	"	"	3×10^{-3}	27
14	"	"	8×10^{-3}	25
15	"	"	2×10^{-2}	22
16	1.00	2-80	4×10^{-4}	30
17	"	"	7×10^{-4}	29
18	"	"	2×10^{-3}	27
19	"	"	4×10^{-3}	25
20	"	"	1×10^{-2}	22
21	"	2-26	6×10^{-4}	29
22	"	"	8×10^{-4}	28
23	"	"	2×10^{-3}	26
24	"	"	4×10^{-3}	24
25	"	"	1×10^{-2}	21
26	"	2-7	3×10^{-3}	26
27	"	"	5×10^{-3}	24
28	"	"	2×10^{-2}	19

(Table 1-c)

Sample No.	Total gelatin amount per one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Coating trouble	Sensitivity	Drying characteristics	Remarks
1	3.35	5	5	100	1	No
2	"	6	5	100	1	No
3	"	8	5	100	1	No
4	3.15	5	4	105	2	No
5	"	6	5	105	2	No
6	"	8	5	105	2	No
7	3.05	5	2	110	3	No
8	"	6	4	110	3	Yes
9	"	8	5	110	3	Yes
10	"	10	5	110	3	Yes
11	2.90	5	2	120	4	No
12	"	6	4	120	4	Yes
13	"	8	5	120	4	Yes
14	"	10	5	120	4	Yes
15	"	13	5	120	4	Yes
16	2.70	5	1	130	5	No
17	"	6	3	130	5	Yes
18	"	8	4	130	5	Yes
19	"	10	5	130	5	Yes
20	"	13	5	130	5	Yes
21	2.20	5	1	145	5	No
22	"	6	3	145	5	Yes
23	"	8	3	145	5	Yes
24	"	10	4	145	5	Yes
25	"	13	5	145	5	Yes
26	2.10	8	1	150	5	No
27	"	10	2	150	5	No
28	"	15	2	150	5	No

* Difference (between emulsion layer and protective layer)

Yes: Present invention No: Not the invention

Table 2

Sample No.	Total gelatin amount per one side (g/m^2)	Difference in surface tension (dyn/cm)(mN/m)	Sensitivity	
			45 second processing	90 second processing
3	3.35	8	100	120
10	3.05	10	110	130
14	2.90	10	120	135
19	2.70	10	130	145
25	2.20	13	145	155
28	2.10	15	150	160

Example 2

Here are described the preparation of emulsions E-2 to E-6 containing silver halide grains having a multi-layer structure. First, a 3.0N ammoniacal silver nitrate solution and a solution containing 2.0 mole % of potassium iodide and 98.0 mole % of potassium bromide were added according to a double jet method at 45 °C while keeping pAg = 11.0 and pH = 9.0. The rate of addition was gradually accelerated with the growth of grains.

The emulsion obtained was found to be an octahedral monodispersed emulsion comprising grains having an average grain size of 1.05 μm. Furthermore, an ammoniacal silver nitrate solution and a solution of potassium bromide were added according to a double jet method at pAg = 11.0 and pH = 9.0 to form shells comprising silver bromide alone. The emulsion thus obtained was found to be an octahedral monodispersed emulsion comprising grains having an average grain size of 1.10 μm. This emulsion was designated E-2.

Subsequently, octahedral silver iodobromide emulsions containing 5 mole %, 10 mole %, 20 mole % and 30 mole % of silver iodide, respectively, were prepared employing substantially the same preparation method as that for E-2, except that the ratio of potassium iodide to potassium bromide was varied, the core size was varied so as to make the average silver content uniform after the shell formation, and the rate of addition at the initial stage of mixing was controlled so as to give the same grain size. Thereafter, the same procedures as for E-2 were taken to prepare corresponding octahedral monodispersed emulsions comprising grains having an average grain size of 1.10 μm, which were designated as E-3, E-4, E-5 and E-6. Chemical sensitization and coating were carried out on emulsions E-1 to E-6 in the same manner as in Example 1 to obtain samples Nos. 29 to 38 as shown in Table 3 (Table 3-a, -b, -c).

These samples were subjected to the 45 second processing as in Example 1 to determine the sensitivity. Abrasion blackening was also measured in the following manner: samples were moisture-conditioned for 4 hours at 23 °C and 55 % RH, and thereafter scratched with a sapphire stylus having a radius of 0.3 mil (7.6 μm) while continuously varying the load, and developed to indicate the abrasion blackening by the load (g) at which the blackening began to occur. The smaller the value is, the weaker the abrasion blackening is.

The results obtained are shown in Table 3 (Table 3-c). As is clear from Table 3, in the grains having a difference of 10 mole % or more in the iodine content between the core and shell, the abrasion blackening occurs less and also the sensitivity is excellent as the amount of gelatin is smaller, when compared with the grains having a difference of less than 10 mole %.

Table 3:

(Table 3-a)

Sample No.	Emulsion	Silver halide emulsion layer: Gelatin amount per one side (g/m^2)	Surface active agent: Type	Surface active agent: Amount per one side (g/m^2)	Surface tension (dyn/cm) (mN/m)
29	E-2	2.20	1-10	1×10^{-3}	36
30	E-3	"	"	"	"
31	E-4	"	"	"	"
32	E-5	"	"	"	"
33	E-6	"	"	"	"
34	E-2	1.70	"	2×10^{-3}	35
35	E-3	"	"	"	"
36	E-4	"	"	"	"
37	E-5	"	"	"	"
38	E-6	"	"	"	"

(Table 3-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Protective layer: Surface active agent: Type	Protective layer: Surface active agent: Amount per one side (g/m^2)	Protective layer: Surface tension (dyn/cm) (mN/m)
29	1.15	1-10	1×10^{-3}	28
30	"	"	"	"
31	"	"	"	"
32	"	"	"	"
33	"	"	"	"
34	1.00	2-80	4×10^{-3}	25
35	"	"	"	"
36	"	"	"	"
37	"	"	"	"
38	"	"	"	"

(Table 3-c)

Sample No.	Total gelatin amount per one side (g/m^2)	Diff. in surface tension (between emulsion layer and protective layer (dyn/cm) (~ N/m)	Sensitivity	Abrasion blackening (g)
29	3.35	8	110	55
30	"	"	110	55
31	"	"	115	58
32	"	"	120	60
33	"	"	125	60
34	2.70	10	140	30
35	"	"	140	33
36	"	"	150	45
37	"	"	155	50
38	"	"	160	55

Example 3

Emulsions containing core grains were prepared by the same procedure as that for E-3 to E-6. Octahedral silver iodobromide emulsions containing 5 mole %, 10 mole %, 20 mole % and 30 mole % of silver iodide were obtained. In the same procedure as that for E-2, except that 2.0 mole % of shell potassium iodide was contained in each of these emulsions, there were prepared corresponding octahedral monodispersed core/shell emulsions comprising grains having an average grain size of 1.10 μm, which were designated E-7, E-8, E-9 and E-10 respectively.

On these monodispersed emulsions, chemical sensitization and coating were carried out in the same manner as in Example 1 to obtain samples No. 39 to No. 46 shown in Table 4 (Table 4-a, -b, -c). On these samples, the abrasion blackening and sensitivity were determined in the same manner as in Example 2 to obtain the results shown in Table 4 (Table 4-c).

As is clear from Table 4, in the grains having a difference of 10 mole % or more in the iodine content between the core and shell, the abrasion blackening occurs less and also the sensitivity is excellent as the

amount of gelatin is smaller, when compared with the grains having a difference of less than 10 mole %.

Table 4:

(Table 4-a)

Sample No.	Emulsion	Silver halide emulsion layer: Gelatin amount per one side (g/m^2)	Surface active agent: Type	Surface active agent: Amount per one side (g/m^2)	Surface tension (dyn/cm) (mN/m)
39	E-7	2.20	1-10	1×10^{-3}	36
40	E-8	"	"	"	"
41	E-9	"	"	"	"
42	E-10	"	"	"	"
43	E-7	1.70	"	2×10^{-3}	35
44	E-8	"	"	"	"
45	E-9	"	"	"	"
46	E-10	"	"	"	"

(Table 4-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Protective layer: Surface active agent: Type	Protective layer: Surface active agent: Amount per one side (g/m^2)	Surface tension (dyn/cm) (mN/m)
39	1.15	1-10	1×10^{-3}	28
40	"	"	"	"
41	"	"	"	"
42	"	"	"	"
43	1.00	2-80	4×10^{-3}	25
44	"	"	"	"
45	"	"	"	"
46	"	"	"	"

(Table 4-c)

Sample No.	Total gelatin amount per one side (g/m^2)	Diff. in surface tension (between emulsion layer and protective layer (dyn/cm) (mN/m)	Sensitivity	Abrasion blackening (g)
39	3.35	8	115	55
40	"	"	120	55
41	"	"	125	58
42	"	"	130	60
43	2.70	10	145	30
44	"	"	150	35
45	"	"	160	50
46	"	"	165	55

Example 4

A cubic monodispersed emulsion comprising silver iodobromide grains having an average grain size of 0.28 μm and containing 2.5 mole % of silver iodide was prepared according to a double jet method while controlling the temperature to be 60° C, pAg = 8.0 and pH = 2.0. Part of this emulsion was used as cores, and allowed to grow in the following manner. To the solutions containing the core grains and gelatin, an ammoniacal silver nitrate solution and a solution containing potassium iodide and potassium bromide were added at 40° C, pAg 8.0 and pH 9.5 according to a double jet method to form a first coat each containing 5 mole %, 10 mole %, 20 mole % or 30 mole % of silver iodide.

Each of the emulsions was treated by the same procedure as that for E-2, except that the pAg was 9.0, to form a second coat comprising silver bromide alone, thereby preparing core/shell emulsions comprising cubic monodispersed silver iodobromide grains having an average grain size of 1.0 μm, which were designated as E-11, E-12, E-13 and E-14, respectively. All of these emulsions had an average silver iodide content of 3.0 mole %.

On these monodispersed emulsions, chemical sensitization and coating were carried out in the same manner as in Example 1 to obtain samples No. 47 to No. 54 shown in Table 5 (Table 5-a, -b, -c). On these samples the abrasion blackening and sensitivity were determined in the same manner as in Example 2 to obtain the results shown in Table 5 (Table 5-c).

As is clear from Table 5 (Table 5-a, -b, -c), in the grains having a difference of 10 mole % or more in the iodine content between the core and shell, the abrasion blackening occurs less and also the sensitivity

is excellent as the amount of gelatin is smaller, when compared with the grains having a difference of less than 10 mole %.

Table 5:

(Table 5-a)

Sample No.	Emulsion	Silver halide emulsion layer: Gelatin amount per one side (g/m^2)	Surface active agent: Type	Surface active agent: Amount per one side (g/m^2)	Surface tension (dyn/cm) (mN/m)
47	E-11	2.20	1-10	1×10^{-3}	36
48	E-12	"	"	"	"
49	E-13	"	"	"	"
50	E-14	"	"	"	"
51	E-11	1.70	"	2×10^{-3}	35
52	E-12	"	"	"	"
53	E-13	"	"	"	"
54	E-14	"	"	"	"

(Table 5-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Protective layer: Surface active agent: Type	Protective layer: Surface active agent: Amount per one side (g/m^2)	Protective layer: Surface tension (dyn/cm) (mN/m)
47	1.15	1-10	1×10^{-3}	28
48	"	"	"	"
49	"	"	"	"
50	"	"	"	"
51	1.00	2-80	4×10^{-3}	25
52	"	"	"	"
53	"	"	"	"
54	"	"	"	"

(Table 5-c)

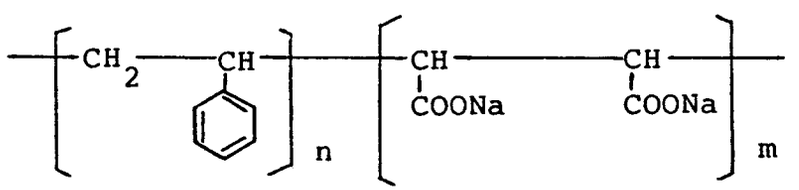
Sample No.	Total gelatin amount per one side (g/m^2)	Diff. in surface tension (between emulsion layer and protective layer (dyn/cm) (mN/m)	Sensitivity	Abrasion blackening (g)
47	3.35	8	120	55
48	"	"	125	58
49	"	"	130	60
50	"	"	135	60
51	2.70	10	150	35
52	"	"	160	50
53	"	"	165	55
54	"	"	170	60

Example 5

Example 1 was repeated to prepare emulsion E-15, except that the thickening agents and surface active agents mentioned below were used. Using this emulsion E-15, chemical sensitization and coating were carried out by the same procedure as in Example 1 to obtain samples No. 55 to No. 110. Subsequently experiments were carried out in the same manner as in Example 1. The results are shown in Tables 6 and 7.

Thickening agents:

(A)



(B) Colloid silica (Ludox AM, produced by Dupont)

The surface active agents used were surface active agents 1-10, 2-26, 2-80 and 3-3 hereinbefore defined and the following compounds (1) to (3).

(1) $NaO_3S-CH(CH_2-COOC_5H_{11})-COOC_5H_{11}$

(2) $F_{19}C_9O-(-CH_2CH_2O-)_{20}-CH_3$

(3) $F_{15}C_7CON(C_3H_7)-(-CH_2CH_2O-)_2-(-CH_2-)_3-SO_3Na$

As is clear from Table 6 (Table 6-a, -b, -c) and Table 7, the samples (light-sensitive silver halide photographic materials) of this invention have good coating properties and also excellent sensitivity and drying characteristics, and thus are suitable for ultra rapid processing. It is also seen from the comparison with the conventional 90 second processing that the processing time can be shortened to 1/2 to provide twice the processing ability, retaining the sensitivity attained in the conventional system.

Example 5 was repeated except for employing dextran in place of the compound (A) as a thickening agent in the emulsion layer. The same result as in Example 5 was observed.

Example 5 was again repeated except for changing the melting time to 20 minutes. The same result was observed.

Table 6:

(Table 6-a)

Sample No.	Silver halide emulsion layer				
	Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pas)
55	2.20	(1)	36	(A)	24
56	2.20	(1)	36	(A)	10
57	2.20	(1)	36	(A)	24
58	2.20	(1)	36	(A)	10
59	2.00	(1)	36	(A)	24
60	2.00	(1)	36	(A)	10
61	2.00	(1)	36	(A)	24
62	2.00	(1)	36	(A)	20
63	1.90	(1)	36	(A)	24
64	1.90	(1)	36	(A)	20
65	1.90	(1)	36	(A)	10
66	1.90	(1)	36	(A)	12
67	1.90	(1)	36	(A)	24
68	1.90	(1)	36	(A)	20
69	1.90	(1)	36	(A)	10
70	1.90	(1)	36	(A)	12
71	1.75	(1)	35	(A)	24
72	1.75	(1)	35	(A)	20
73	1.75	(1)	35	(A)	10
74	1.75	(1)	35	(A)	12
75	1.75	(1)	35	(A)	24
76	1.75	(1)	35	(A)	20
77	1.75	(1)	35	(A)	10
78	1.75	(1)	35	(A)	12
79	1.75	(1)	35	(A)	24
80	1.75	(1)	35	(A)	20
81	1.75	(1)	35	(A)	10
82	1.75	(1)	35	(A)	12

(Table 6-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pa·s)
55	1.15	1-10	30	(B)	22
56	1.15	1-10	30	(B)	10
57	1.15	1-10	31	(B)	22
58	1.15	1-10	31	(B)	10
59	1.15	3-3	30	(B)	22
60	1.15	3-3	30	(B)	10
61	1.15	3-3	31	(B)	22
62	1.15	3-3	31	(B)	20
63	1.15	(1)	30	(B)	22
64	1.15	(1)	30	(B)	20
65	1.15	(1)	30	(B)	12
66	1.15	(1)	30	(B)	10
67	1.15	(1)	31	(B)	20
68	1.15	(1)	31	(B)	20
69	1.15	(1)	31	(B)	12
70	1.15	(1)	31	(B)	10
71	1.15	(2)	29	(B)	22
72	1.15	(2)	29	(B)	20
73	1.15	(2)	29	(B)	12
74	1.15	(2)	29	(B)	10
75	1.15	(2)	30	(B)	22
76	1.15	(2)	30	(B)	20
77	1.15	(2)	30	(B)	12
78	1.15	(2)	30	(B)	10
79	1.15	(2)	27	(B)	22
80	1.15	(2)	27	(B)	20
81	1.15	(2)	27	(B)	12
82	1.15	(2)	27	(B)	10

(Table 6-c)

Sample No.	Total gelatin amount/ one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Diff.* in viscosity (cp) ($\times 10^{-3}$ Pas)	Coating trouble	Sensitivity	Drying characteristics	Remarks
55	3.35	6	2	5	100	1	No
56	3.35	6	0	5	100	1	No
57	3.35	5	2	5	100	1	No
58	3.35	5	0	5	100	1	No
59	3.15	6	2	5	105	2	No
60	3.15	6	0	5	105	2	No
61	3.15	5	2	4	105	2	No
62	3.15	5	0	4	105	2	No
63	3.05	6	2	2	110	3	No
64	3.05	6	0	4	110	3	Yes
65	3.05	6	-2	5	110	3	Yes
66	3.05	6	2	5	110	3	Yes
67	3.05	5	2	2	110	3	No
68	3.05	5	0	2	110	3	No
69	3.05	5	-2	2	110	3	No
70	3.05	5	2	2	110	3	No
71	2.90	6	2	2	120	4	No
72	2.90	6	0	4	120	4	Yes
73	2.90	6	-2	5	120	4	Yes
74	2.90	6	2	5	120	4	Yes
75	2.90	5	2	2	120	4	No
76	2.90	5	0	2	120	4	No
77	2.90	5	-2	2	120	4	No
78	2.90	5	2	2	120	4	No
79	2.90	8	2	2	120	4	No
80	2.90	8	0	4	120	4	Yes
81	2.90	8	-2	5	120	4	Yes
82	2.90	8	2	5	120	4	Yes

* Difference (between emulsion layer and protective layer)

Yes: Present invention No: Not the invention

Table 6 (cont'd)

(Table 6-a, cont'd)

Sample No.	Silver halide emulsion layer				
	Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pa·s)
83	1.70	(1)	35	(A)	24
84	1.70	(1)	35	(A)	20
85	1.70	(1)	35	(A)	10
86	1.70	(1)	35	(A)	12
87	1.70	(1)	35	(A)	24
88	1.70	(1)	35	(A)	20
89	1.70	(1)	35	(A)	10
90	1.70	(1)	35	(A)	12
91	1.70	(1)	35	(A)	24
92	1.70	(1)	35	(A)	20
93	1.70	(1)	35	(A)	10
94	1.70	(1)	35	(A)	12
95	1.20	(1)	34	(A)	24
96	1.20	(1)	34	(A)	20
97	1.20	(1)	34	(A)	10
98	1.20	(1)	34	(A)	12
99	1.20	(1)	34	(A)	24
100	1.20	(1)	34	(A)	20
101	1.20	(1)	34	(A)	10
102	1.20	(1)	34	(A)	12
103	1.20	(1)	34	(A)	24
104	1.20	(1)	34	(A)	20
105	1.20	(1)	34	(A)	10
106	1.20	(1)	34	(A)	12
107	1.10	(1)	34	(A)	24
108	1.10	(1)	34	(A)	10
109	1.10	(1)	34	(A)	24
110	1.10	(1)	34	(A)	10

(Table 6-b, cont'd)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pas)
83	1.00	2-80	29	(B)	22
84	1.00	"	29	(B)	20
85	1.00	"	29	(B)	12
86	1.00	"	29	(B)	10
87	1.00	"	30	(B)	22
88	1.00	"	30	(B)	20
89	1.00	"	30	(B)	12
90	1.00	"	30	(B)	10
91	1.00	"	27	(B)	22
92	1.00	"	27	(B)	20
93	1.00	"	27	(B)	12
94	1.00	"	27	(B)	10
95	1.00	2-26	28	(B)	22
96	1.00	"	28	(B)	20
97	1.00	"	28	(B)	12
98	1.00	"	28	(B)	10
99	1.00	"	29	(B)	22
100	1.00	"	29	(B)	20
101	1.00	"	29	(B)	12
102	1.00	"	29	(B)	10
103	1.00	"	26	(B)	22
104	1.00	"	26	(B)	20
105	1.00	"	26	(B)	12
106	1.00	"	26	(B)	10
107	1.00	(3)	28	(B)	22
108	1.00	"	28	(B)	10
109	1.00	"	26	(B)	22
110	1.00	"	26	(B)	10

(Table 6-c, cont'd)

Sample No.	Total gelatin amount/ one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Diff.* in viscosity (cp) ($\times 10^{-3}$ Pas)	Coating trouble	Sensitivity	Drying characteristics	Remarks
83	2.70	6	2	2	130	5	No
84	2.70	6	0	4	130	5	Yes
85	2.70	6	-2	5	130	5	Yes
86	2.70	6	2	5	130	5	Yes
87	2.70	5	2	1	130	5	No
88	2.70	5	0	1	130	5	No
89	2.70	5	-2	1	130	5	No
90	2.70	5	2	1	130	5	No
91	2.70	8	2	1	130	5	No
92	2.70	8	0	4	130	5	Yes
93	2.70	8	-2	5	130	5	Yes
94	2.70	8	2	5	130	5	Yes
95	2.20	6	2	2	145	5	No
96	2.20	6	0	3	145	5	Yes
97	2.20	6	-2	4	145	5	Yes
98	2.20	6	2	4	145	5	Yes
99	2.20	5	2	1	145	5	No
100	2.20	5	0	1	145	5	No
101	2.20	5	-2	1	145	5	No
102	2.20	5	2	1	145	5	No
103	2.20	8	2	2	145	5	No
104	2.20	8	0	3	145	5	Yes
105	2.20	8	-2	4	145	5	Yes
106	2.20	8	2	4	145	5	Yes
107	2.10	6	2	1	150	5	No
108	2.10	6	0	1	150	5	No
109	2.10	8	2	1	150	5	No
110	2.10	8	0	1	150	5	No

* Difference (between emulsion layer and protective layer)

Yes: Present invention No: Not the invention

Table 7

Sample No.	Total gelatin amount per one side (g/m^2)	Diff. in surface tension (dyn/cm) (mN/m)	Diff. in viscosity	Sensitivity	
				45 second processing	90 second processing
56	3.35	6	0	100	120
60	3.15	6	0	105	125
64	3.05	6	0	110	130
72	2.90	6	0	120	135
84	2.70	6	0	130	145
96	2.20	6	0	145	155
106	2.10	6	0	150	160

Example 6

Example 2 was repeated to prepare emulsions E-16 to E-20, except that the thickening agents and surface active agents used in Example 5 were used. Chemical sensitization and coating were carried out by same procedures as in Example 2 to obtain samples No. 111 to No. 120 shown hereinbelow. Experiments were carried out on these samples in the same manner as in Example 2. The results obtained are shown in Table 8 (Table 8-a, -b, -c).

As is clear from Table 8, in the grains having a difference of 10 mole % or more in the iodine content between the core and shell, the abrasion blackening occurs less and also the sensitivity is excellent as the amount of gelatin is smaller, when compared with the grains having a difference of less than 10 mole %.

Table 8:

(Table 8-a)

Sample No.	Emulsion	Silver halide emulsion layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pa·s)
111	E-16	2.20	(1)	36	(A)	10
112	E-17	2.20	(1)	36	(A)	10
113	E-18	2.20	(1)	36	(A)	10
114	E-19	2.20	(1)	36	(A)	10
115	E-20	2.20	(1)	36	(A)	10
116	E-16	1.70	(1)	35	(A)	10
117	E-17	1.70	(1)	35	(A)	10
118	E-18	1.70	(1)	35	(A)	10
119	E-19	1.70	(1)	35	(A)	10
120	E-20	1.70	(1)	35	(A)	10

(Table 8-b)

Sample No.	Protective layer				
	Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pa s)
111	1.15	(1)	30	(B)	10
112	1.15	(1)	30	(B)	10
113	1.15	(1)	30	(B)	10
114	1.15	(1)	30	(B)	10
115	1.15	(1)	30	(B)	10
116	1.00	2-80	27	(B)	10
117	1.00	"	27	(B)	10
118	1.00	"	27	(B)	10
119	1.00	"	27	(B)	10
120	1.00	"	27	(B)	10

(Table 8-c)

Sample No.	Total gelatin amount per one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Diff.* in viscosity (cp) ($\times 10^{-3}$ Pa·s)	Sensitivity	Abrasion blackening (g)
111	3.35	6	0	110	55
112	3.35	6	0	110	55
113	3.35	6	0	115	58
114	3.35	6	0	120	60
115	3.35	6	0	125	60
116	2.70	8	0	140	30
117	2.70	8	0	140	33
118	2.70	8	0	150	45
119	2.70	8	0	155	50
120	2.70	8	0	160	55

* Difference (between emulsion layer and protective layer)

Example 7

Emulsions containing core grains were prepared by the same procedures as those for E-17 to E-20, whereby octahedral silver iodobromide emulsions containing 5 mole %, 10 mole %, 20 mole % and 30 mole % of silver iodide, respectively, were obtained. In the same procedure as that for E-16, except that 2.0 mole % of shell potassium iodide was contained in each of these emulsions, there were prepared corresponding tetrahedral monodispersed core/shell emulsions comprising grains having an average grain size of 1.10 μm, which were designated as E-21, E-22, E-23 and E-24, respectively.

On these monodispersed emulsions, chemical sensitization and coating were carried out in the same manner as in Example 5 to obtain samples No. 121 to No. 128 shown in Table 9 (Table 9-a, -b, c) below. On these samples, abrasion blackening and sensitivity were determined in the same manner as in Example 6 to obtain the results shown in Table 9 (Table 9-c).

As is clear from Table 9, in the grains having a difference of 10 mole % or more in the iodine content between the core and shell, the abrasion blackening occurs less and also the sensitivity is excellent as the amount of gelatin is smaller, when compared with the grains having a difference of less than 10 mole %.

Table 9:

(Table 9-a)

Sample No.	Emulsion	Silver halide emulsion layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pas)
121	E-21	2.20	(1)	36	(A)	10
122	E-22	2.20	(1)	36	(A)	10
123	E-23	2.20	(1)	36	(A)	10
124	E-24	2.20	(1)	36	(A)	10
125	E-21	1.70	(1)	35	(A)	10
126	E-22	1.70	(1)	35	(A)	10
127	E-23	1.70	(1)	35	(A)	10
128	E-24	1.70	(1)	35	(A)	10

(Table 9-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pa·s)
121	1.15	(1)	30	(B)	10
122	1.15	(1)	30	(B)	10
123	1.15	(1)	30	(B)	10
124	1.15	(1)	30	(B)	10
125	1.00	2-80	27	(B)	10
126	1.00	"	27	(B)	10
127	1.00	"	27	(B)	10
128	1.00	"	27	(B)	10

(Table 9-c)

Sample No.	Total gelatin amount per one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Diff.* in viscosity (cp) ($\times 10^{-3}$ Pa s)	Sensitivity	Abrasion blackening (g)
121	3.35	6	0	115	55
122	3.35	6	0	120	55
123	3.35	6	0	125	58
124	3.35	6	0	130	60
125	2.70	8	0	145	30
126	2.70	8	0	150	35
127	2.70	8	0	160	50
128	2.70	8	0	165	55

* Difference (between emulsion layer and protective layer)

Example 8

Example 4 was repeated to prepare emulsions E-25 to E-28, except that the thickening agents and surface active agents used in Example 5 were used. Chemical sensitization and coating were carried out on these samples by the same procedures as in Example 4 to obtain samples No. 129 to No. 136 as shown in Table 10 (Table 10-a, -b, -c). Experiments were carried out in the same manner as in Example 4 to obtain the results shown in Table 10 (Table 10-c).

As is clear from Table 10 (Table 10-a, -b, -c), in the grains having a difference of 10 mole % or more in the iodine content between the core and shell, the abrasion blackening occurs less and also the sensitivity is excellent as the amount of gelatin is smaller.

Table 10:

(Table 10-a)

Sample No.	Emulsion	Silver halide emulsion layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pa·s)
129	E-25	2.20	(1)	36	(A)	10
130	E-26	2.20	(1)	36	(A)	10
131	E-27	2.20	(1)	36	(A)	10
132	E-28	2.20	(1)	36	(A)	10
133	E-25	1.70	(1)	35	(A)	10
134	E-26	1.70	(1)	35	(A)	10
135	E-27	1.70	(1)	35	(A)	10
136	E-28	1.70	(1)	35	(A)	10

(Table 10-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pa·s)
129	1.15	(1)	30	(B)	10
130	1.15	(1)	30	(B)	10
131	1.15	(1)	30	(B)	10
132	1.15	(1)	30	(B)	10
133	1.00	(1)	27	(B)	10
134	1.00	(1)	27	(B)	10
135	1.00	(1)	27	(B)	10
136	1.00	(1)	27	(B)	10

(Table 10-c)

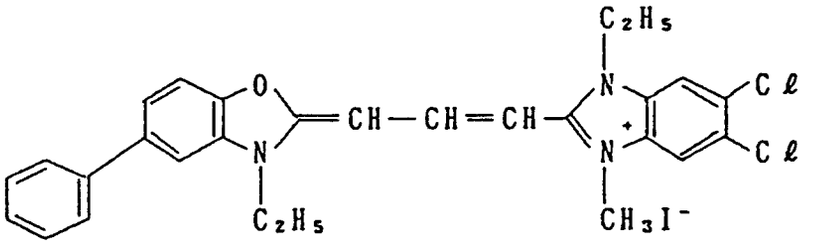
Sample No.	Total gelatin amount per one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Diff.* in viscosity (cp) ($\times 10^{-3}$ Pas)	Sensitivity	Abrasion blackening (g)
129	3.35	6	0	120	55
130	3.35	6	0	125	58
131	3.35	6	0	130	60
132	3.35	6	0	135	60
133	2.70	8	0	150	35
134	2.70	8	0	160	50
135	2.70	8	0	165	55
136	2.70	8	0	170	60

* Difference (between emulsion layer and protective layer)

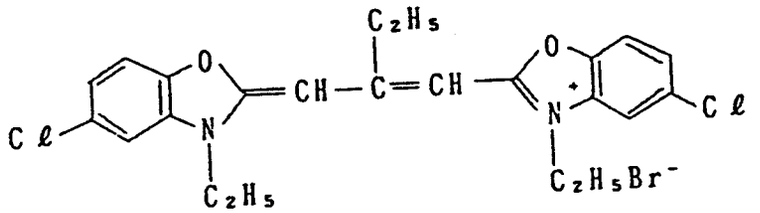
Example 9

In this example, using the emulsion used in Example 5, the sensitizing dyes shown as the examples of the compounds of Formulas (I) to (III) or control dyes (a) to (c) shown below were added. Thereafter, chloroauric acid, sodium thiosulfate and ammonium thiocyanate were added to carry out optimum gold and sulfur sensitization, followed by stablization with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene. The silver coating weight was 45 mg/dm^2, and conditions which were otherwise the same as in the procedures in Example 5 were used to obtain samples No. 137 to No. 197 as in Table 11 (Table 11-a, -b, -c) shown below. On these samples, coating problems, sensitivities and drying characteristics were evaluated in the same manner as in Example 5 to obtain the results shown in Table 12 below.

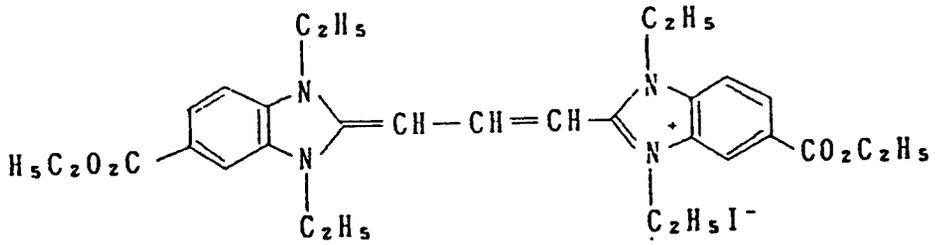
Control dye (a)



Control dye (b)



Control dye (c)



R.M.S. granularity was also measured in the following manner.

Each sample was inserted in an orthochromatic sensitizing screen KS (produced by Konishiroku Photo Industry Co., Ltd.), and irradiated with X-rays for 0.10 second at a tube voltage of 90 KVP and a tube current of 100 mA with an aluminum wedge, followed by the above 45 second processing. Subsequently, an emulsion layer of the sample was peeled off at a portion having a density of 1.0 and, at the front side facing an X-ray generator and using Sakura one-touch type RMS measuring machine (produced by Konishiroku Photo Industry Co., Ltd.), the other side emulsion face was measured under an aperture size of 50 x 200 μm. The smaller the measured value is, the better the granularity is.

Similarly to Example 5, part of the samples were processed to detemine the sensitivity in the conventional 90 second processing by dropping to 1/2 the line speed of the above 45 second automatic processor. The results obtained are shown in Table 13.

As is clear from Table 12 and Table 13, the samples according to this invention have good coating properties and also excellent sensitivity and drying characteristics, and thus are suitable for ultra rapid processing. It is also seen from the comparison with the conventional 90 second processing that the processing time can be shortened to 1/2 to provide twice the processing ability, retaining the sensitivity attained in the conventional system.

Table 11:

(Table 11-a)

Sample No.	Emulsion	Silver halide emulsion layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pa·s)
137	E-15	2.00	(1)	36	(A)	24
138	E-15	2.00	(1)	36	(A)	10
139	E-15	2.00	(1)	36	(A)	24
140	E-15	2.00	(1)	36	(A)	10
141	E-15	1.90	(1)	36	(A)	24
142	E-15	1.90	(1)	36	(A)	20
143	E-15	1.90	(1)	36	(A)	10
144	E-15	1.90	(1)	36	(A)	24
145	E-15	1.90	(1)	36	(A)	20
146	E-15	1.90	(1)	36	(A)	10
147	E-15	1.75	(1)	35	(A)	24
148	E-15	1.75	(1)	35	(A)	20
149	E-15	1.75	(1)	35	(A)	10
150	E-15	1.75	(1)	35	(A)	24
151	E-15	1.75	(1)	35	(A)	20
152	E-15	1.75	(1)	35	(A)	10
153	E-15	1.75	(1)	35	(A)	24
154	E-15	1.75	(1)	35	(A)	20
155	E-15	1.75	(1)	35	(A)	10
156	E-15	1.70	(1)	35	(A)	24
157	E-15	1.70	(1)	35	(A)	20
158	E-15	1.70	(1)	35	(A)	10
159	E-15	1.70	(1)	35	(A)	24
160	E-15	1.70	(1)	35	(A)	20
161	E-15	1.70	(1)	35	(A)	10
162	E-15	1.70	(1)	35	(A)	24

(Table 11-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pa·s)
137	1.15	3-3	30	(B)	22
138	1.15	"	30	(B)	10
139	1.15	"	31	(B)	22
140	1.15	"	31	(B)	10
141	1.15	(1)	30	(B)	22
142	1.15	(1)	30	(B)	20
143	1.15	(1)	30	(B)	10
144	1.15	(1)	31	(B)	22
145	1.15	(1)	31	(B)	20
146	1.15	(1)	31	(B)	10
147	1.15	(2)	29	(B)	22
148	1.15	(2)	29	(B)	20
149	1.15	(2)	29	(B)	10
150	1.15	(2)	30	(B)	22
151	1.15	(2)	30	(B)	20
152	1.15	(2)	30	(B)	10
153	1.15	(2)	27	(B)	22
154	1.15	(2)	27	(B)	20
155	1.15	(2)	27	(B)	10
156	1.10	2-80	29	(B)	22
157	1.10	"	29	(B)	20
158	1.10	"	29	(B)	10
159	1.10	"	30	(B)	22
160	1.10	"	30	(B)	20
161	1.10	"	30	(B)	10
162	1.10	"	27	(B)	22

(Table 11-c)

Sample No.	Total gelatin amount/ one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Diff.* in viscosity (cp) ($\times 10^{-3}$ Pa·s)	Sensitizing dye Type	Sensitizing dye Amount (mg/mole AgX)	Remarks
137	3.15	6	2	(2)	120	No
138	3.15	6	0	(2)	120	No
139	3.15	5	2	(2)	120	No
140	3.15	5	0	(2)	120	No
141	3.05	6	2	(2)	120	No
142	3.05	6	0	(44)	120	Yes
143	3.05	6	0	(74)	120	Yes
144	3.05	5	2	(44)	120	No
145	3.05	5	0	(44)	120	No
146	3.05	5	0	(44)	120	No
147	2.90	6	2	(74)	120	No
148	2.90	6	0	(2)	120	Yes
149	2.90	6	0	(44)	120	Yes
150	2.90	5	2	(44)	120	No
151	2.90	5	0	(2)	120	No
152	2.90	5	0	(74)	120	No
153	2.90	8	2	(44)	120	No
154	2.90	8	0	(2)	120	Yes
155	2.90	8	0	(74)	120	Yes
156	2.70	6	2	(74)	120	No
157	2.70	6	0	(44)	120	Yes
158	2.70	6	0	(2)	120	Yes
159	2.70	5	2	(2)	120	No
160	2.70	5	0	(44)	120	No
161	2.70	5	0	(74)	120	No
162	2.70	8	2	(2)	120	No

* Difference (between emulsion layer and protective layer)

Yes: Present invention No: Not the invention

Table 11 (cont'd):

(Table 11-a, cont'd)

Sample No.	Emulsion	Silver halide emulsion layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pas)
163	E-15	1.70	(1)	35	(A)	20
164	"	1.70	(1)	35	(A)	10
165	"	1.20	(1)	34	(A)	24
166	"	1.20	(1)	34	(A)	20
167	"	1.20	(1)	34	(A)	10
168	"	1.20	(1)	34	(A)	24
169	"	1.20	(1)	34	(A)	20
170	"	1.20	(1)	34	(A)	10
171	"	1.20	(1)	34	(A)	24
172	"	1.20	(1)	34	(A)	10
173	"	1.20	(1)	34	(A)	20
174	"	1.10	(1)	34	(A)	24
175	"	1.10	(1)	34	(A)	10
176	"	1.10	(1)	34	(A)	24
177	"	1.10	(1)	34	(A)	10
178	"	1.70	(1)	35	(A)	24
179	"	1.70	(1)	35	(A)	20
180	"	1.70	(1)	35	(A)	10
181	"	1.70	(1)	35	(A)	24
182	"	1.70	(1)	35	(A)	20
183	"	1.70	(1)	35	(A)	10
184	"	1.70	(1)	35	(A)	24
185	"	1.70	(1)	35	(A)	20
186	"	1.70	(1)	35	(A)	10
187	"	1.90	(1)	36	(A)	24
188	"	1.90	(1)	36	(A)	10

(Table 11-b, cont'd)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pas)
163	1.00	2-80	27	(B)	20
164	1.00	"	27	(B)	10
165	1.00	2-26	28	(B)	22
166	1.00	"	28	(B)	20
167	1.00	"	28	(B)	10
168	1.00	"	29	(B)	22
169	1.00	"	29	(B)	20
170	1.00	"	29	(B)	10
171	1.00	"	26	(B)	22
172	1.00	"	26	(B)	20
173	1.00	"	26	(B)	10
174	1.00	(3)	28	(B)	22
175	1.00	"	28	(B)	10
176	1.00	"	26	(B)	22
177	1.00	"	26	(B)	10
178	1.00	2-80	29	(B)	22
179	1.00	"	29	(B)	20
180	1.00	"	29	(B)	10
181	1.00	"	30	(B)	22
182	1.00	"	30	(B)	20
183	1.00	"	30	(B)	10
184	1.00	"	27	(B)	22
185	1.00	"	27	(B)	20
186	1.00	"	27	(B)	10
187	1.15	1-10	30	(B)	22
188	1.15	"	30	(B)	10

(Table 11-c, cont'd)

Sample No.	Total gelatin amount/ one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Diff.* in viscosity (cp) ($\times 10^{-3}$ Pa·s)	Sensitizing dye Type	Sensitizing dye Amount (mg/mole AgX)	Remarks
163	2.70	8	0	(44)	120	Yes
164	2.70	8	0	(74)	120	Yes
165	2.20	6	2	(44)	120	No
166	2.20	6	0	(74)	120	No
167	2.20	6	0	(2)	120	Yes
168	2.20	5	2	(44)	120	No
169	2.20	5	0	(2)	120	No
170	2.20	5	0	(74)	120	No
171	2.20	8	2	(74)	120	No
172	2.20	8	0	(2)	120	Yes
173	2.20	8	0	(44)	120	Yes
174	2.10	6	2	(74)	120	No
175	2.10	6	0	(74)	120	Yes
176	2.10	8	2	(74)	120	No
177	2.10	8	0	(74)	120	Yes
178	2.70	6	2	(a)	120	No
179	2.70	6	0	(b)	120	Yes
180	2.70	6	0	(c)	120	Yes
181	2.70	5	2	(a)	120	No
182	2.70	5	0	(b)	120	No
183	2.70	5	0	(c)	120	No
184	2.70	8	2	(a)	120	No
185	2.70	8	0	(b)	120	Yes
186	2.70	8	0	(c)	120	Yes
187	3.05	6	2	(a)	120	No
188	3.05	6	0	(b)	120	Yes

* Difference (between emulsion layer and protective layer)

Yes: Present invention No: Not the invention

Table 11 (cont'd):

(Table 11-a, cont'd)

Sample No.	Emulsion	Silver halide emulsion layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pa·s)
189	E-15	1.90	(1)	36	(A)	24
190	"	1.90	(1)	36	(A)	10
191	"	1.20	(1)	34	(A)	24
192	"	1.20	(1)	34	(A)	10
193	"	1.20	(1)	34	(A)	24
194	"	1.20	(1)	34	(A)	10
195	"	1.70	(1)	35	(A)	24
196	"	1.70	(1)	35	(A)	20
197	"	1.70	(1)	35	(A)	10

(Table 11-b, cont'd)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pas)
189	1.15	1-10	31	(B)	22
190	1.15	"	31	(B)	10
191	1.00	2-26	28	(B)	22
192	1.00	"	28	(B)	10
193	1.00	"	29	(B)	22
194	1.00	"	29	(B)	10
195	1.00	2-80	29	(B)	22
196	1.00	"	29	(B)	20
197	1.00	"	29	(B)	10

(Table 11-c, cont'd)

Sample No.	Total gelatin amount/ one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Diff.* in viscosity (cp) ($\times 10^{-3}$ Pa·s)	Sensitizing dye Type	Sensitizing dye Amount (mg/mole AgX)	Remarks
189	3.05	5	2	(b)	120	No
190	3.05	5	0	(c)	120	No
191	2.20	6	2	(c)	120	No
192	2.20	6	0	(a)	120	Yes
193	2.20	5	2	(a)	120	No
194	2.20	5	0	(b)	120	No
195	2.70	6	2	None	-	No
196	2.70	6	0	None	-	Yes
197	2.70	6	0	None	-	Yes

* Difference (between emulsion layer and protective layer)

Yes: Present invention No: Not the invention

Table 12

Sample No.	Coating trouble	Sensitivity	Drying characteristic	Granularity	Remarks
137	5	150	2	0.0017	No
138	5	150	2	0.0017	No
139	5	150	2	0.0017	No
140	5	150	2	0.0017	No
141	2	160	3	0.0018	No
142	4	155	3	0.0018	Yes
143	5	155	3	0.0018	Yes
144	2	155	3	0.0018	No
145	2	155	3	0.0018	No
146	2	155	3	0.0018	No
147	2	165	4	0.0019	No
148	4	170	4	0.0019	Yes
149	5	165	4	0.0019	Yes
150	2	165	4	0.0019	No
151	2	170	4	0.0019	No
152	2	165	4	0.0019	No
153	2	165	4	0.0019	No
154	4	170	4	0.0019	Yes
155	5	165	4	0.0020	Yes
156	2	175	5	0.0020	No
157	3	180	5	0.0020	Yes
158	4	175	5	0.0020	Yes
159	1	180	5	0.0020	No
160	1	175	5	0.0020	No
161	1	175	5	0.0020	No
162	1	180	5	0.0020	No
163	4	175	5	0.0020	Yes
164	5	175	5	0.0021	Yes
165	1	190	5	0.0021	No
166	3	190	5	0.0021	Yes

Yes: Present invention No: Not the invention

Table 12 (cont'd)

Sample No.	Coating trouble	Sensitivity	Drying characteristic	Garanularity	Remarks
167	4	195	5	0.0021	No
168	1	190	5	0.0021	No
169	1	195	5	0.0021	No
170	1	190	5	0.0021	No
171	1	190	5	0.0021	No
172	4	195	5	0.0021	Yes
173	5	190	5	0.0021	Yes
174	1	195	5	0.0022	No
175	3	195	5	0.0022	Yes
176	1	195	5	0.0022	No
177	3	195	5	0.0022	Yes
178	1	135	5	0.0020	No
179	3	135	5	0.0020	Yes
180	4	135	5	0.0020	Yes
181	1	135	5	0.0020	No
182	1	135	5	0.0020	No
183	1	135	5	0.0020	No
184	1	135	5	0.0020	No
185	2	135	5	0.0020	No
186	2	135	5	0.0020	No
187	2	105	3	0.0018	No
188	2	105	3	0.0018	No
189	2	105	3	0.0018	No
190	2	105	3	0.0018	No
191	1	150	5	0.0021	No
192	3	150	5	0.0021	Yes
193	1	150	5	0.0021	No
194	1	150	5	0.0021	No
195	1	130	5	0.0020	No
196	3	130	5	0.0020	Yes
197	3	130	5	0.0020	Yes

Yes: Present invention No: Not the invention

Table 13

Sample No.	Total gelatin amount per one side (g/m^2)	Diff. in surface tension (dyn/cm) (mN/m)	Diff. in viscosity	Sensitizing dye	Sensitivity	
					45 s processing	90 s processing
138	3.15	6	0	(2)	150	170
143	3.05	6	0	(74)	155	175
149	2.90	6	0	(44)	165	180
158	2.70	6	0	(2)	175	190
167	2.20	6	0	(2)	195	205
175	2.10	6	0	(74)	195	205
180	2.70	6	0	(c)	135	140
188	3.05	6	0	(b)	105	115
192	2.20	6	0	(a)	150	155

Example 10

Using the emulsion used in Example 6, the sensitizing dyes (2) were added, and thereafter, chloroauric acid, sodium thiosulfate and ammonium thiocyanate were added to carry out optimum gold and sulfur sensitization, followed by stabilization with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene. The silver coating weight was 45 mg/dm^2, and other conditions were the same as in the procedures in Example 5. The samples shown in Table 14 (Table 14-a, -b, -c) below were obtained.

On these samples, experiments were carried out in the same manner as in Example 6 to obtain the results shown in Table 15 below.

As is clear from Table 15, in the grains having a difference of 10 mole % or more in the iodine content between the core and shell, the abrasion blackening occurs less and also the sensitivity is excellent as the amount of gelatin is smaller, when compared with the grains having a difference of less than 10 mole %.

Similar experiments were carried out using sensitizing dyes (44) and (74) to obtain similar results.

Table 14:

(Table 14-a)

Sample No.	Emulsion	Silver halide emulsion layer: Gelatin amount per one side (g/m^2)	Type of surface active agent	Surface tension (dyn/cm) (mN/m)	Type of thickening agent	Viscosity (cp) ($\times 10^{-3}$ Pas)
198	E-16	2.00	(1)	36	(A)	10
199	E-17	2.00	(1)	36	(A)	10
200	E-18	2.00	(1)	36	(A)	10
201	E-19	2.00	(1)	36	(A)	10
202	E-20	2.00	(1)	36	(A)	10
203	E-16	1.70	(1)	35	(A)	10
204	E-17	1.70	(1)	35	(A)	10
205	E-18	1.70	(1)	35	(A)	10
206	E-19	1.70	(1)	35	(A)	10
207	E-20	1.70	(1)	35	(A)	10

(Table 14-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Protective layer: Type of surface active agent	Protective layer: Surface tension (dyn/cm) (mN/m)	Protective layer: Type of thickening agent	Protective layer: Viscosity (cp) ($\times 10^{-3}$ Pa·s)
198	1.15	3-3	30	(B)	10
199	1.15	"	30	(B)	10
200	1.15	"	30	(B)	10
201	1.15	"	30	(B)	10
202	1.15	"	30	(B)	10
203	1.00	2-80	29	(B)	10
204	1.00	"	29	(B)	10
205	1.00	"	29	(B)	10
206	1.00	"	29	(B)	10
207	1.00	"	29	(B)	10

(Table 14-c)

Sample No.	Total gelatin amount/ one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Diff.* in viscosity (cp) ($\times 10^{-3}$ Pas)	Sensitizing dye Type	Sensitizing dye Amount (mg/mole AgX)
198	3.15	6	0	(2)	120
199	3.15	6	0	(2)	120
200	3.15	6	0	(2)	120
201	3.05	6	0	(2)	120
202	3.05	6	0	(2)	120
203	2.70	6	0	(2)	120
204	2.70	6	0	(2)	120
205	2.70	6	0	(2)	120
206	2.70	6	0	(2)	120
207	2.70	6	0	(2)	120

* Difference (between emulsion layer and protective layer)

Table 15

Sample No.	Sensitivity	Abrasion blackening
198	160	58
199	165	58
200	170	61
201	175	63
202	180	63
203	185	33
204	190	36
205	195	48
206	200	53
207	205	58

Example 11

Two kinds of silver iodobromide emulsions containing 3.0 mole % of silver iodide were prepared by regular mixing in a full ammonia method. They comprised grains having an average grain size of 1.10 μm and 0.80 μm, which are designated as emulsions E-29 and E-30, respectively. To these emulsions E-29 and E-30, the sensitizing dyes shown in Table 16 (Table 16-c) were added. Thereafter, chloroauric acid, sodium thiosulfate and ammonium thiocyanate were added to carry out optimum gold and sulfur sensitization, followed by stabilization with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene.

Both sides of a polyester film support having been subjected to a subbing treatment were coated, together with the above emulsions, with a protective layer to which a hardening agent was added, to provide layers in the order of the silver halide emulsion layer and the protective layer according to a slide hopper method at a coating rate of 100 m/min so that two layers simultaneously overlap, thereby obtaining Samples No. 208 to No. 230. The amount of gelatin, surface active agents, difference in surface tension and sensitizing dyes are shown in Table 16 (Table 16-a, -b, -c) with use of reference to the above-mentioned exemplary compound No. (and control dye No. shown below).

The silver weight was 45 mg/dm^2.

The amount of hardening agent in each of the above samples was controlled such that the melting time was about 30 minutes.

In measuring the R.M.S. granularity, the sample to which no sensitizing dye was added was inserted in a regular sensitizing screen NS (produced by Konishiroku Photo Industry Co., Ltd.) and the sample to which the sensitizing dye was added was inserted in an orthochromatic sensitizing screen KS (produced by Konishiroku Photo Industry Co., Ltd.).

Measurement of pressure desensitization was carried out in the following manner. Each sample was moisture-conditioned at 23° C, 35 % R.H. for 5 hours, and, under such conditions, folded about 280° with a curvature radius of 2 cm. Three (3) minutes after being folded the sample was exposed with an optical wedge for 1/10 second using a tungsten lamp as a light source to carry out development. The difference in density between the portion with a blackening density of 1.0 where desensitization occurred due to the folding and the density of 1.0 at the portion where the sample was not folded, was indicated by ΔD. It follows that, the smaller this value is, the smaller the pressure desensitization is.

The results obtained are shown in Table 17.

Part of the samples was also processed to obtain the sensitivity in a conventional 90 second processing by dropping to 1/2 the line speed of the above 45 second automatic processor. The results are shown in Table 18.

As is clear from Table 17 and Table 18, the samples according to this invention have good coating properties and also excellent sensitivity, granularity, pressure desensitization, abrasion blackening and drying characteristics, and thus are suitable for ultra rapid processing. It is also seen by comparison with the conventional 90 second processing that the sensitivity is higher than the conventional system, and yet the processing time can be shortened to 1/2 to provide twice the processing ability.

Table 16:

(Table 16-a)

Sample No.	Silver halide emulsion layer				
	Emulsion	Gelatin amount per one side (g/m^2)	Surface active agent Type	Surface active agent Amount per one side (g/m^2)	Surface tension (dyn/cm) (mN/m)
208	E-29	1.60	1-5	2×10^{-4}	35
209	E-30	2.10	1-5	2×10^{-4}	35
210	E-30	2.10	1-5	2×10^{-4}	35
211	E-30	2.10	1-5	2×10^{-4}	35
212	E-30	2.00	1-5	2×10^{-4}	35
213	E-30	2.00	1-5	2×10^{-4}	35
214	E-30	2.00	1-5	2×10^{-4}	35
215	E-30	1.60	1-5	2×10^{-4}	35
216	E-30	1.60	1-5	2×10^{-4}	35
217	E-30	1.60	1-5	2×10^{-4}	35
218	E-30	1.60	1-5	2×10^{-4}	35
219	E-30	1.60	1-5	2×10^{-4}	35
220	E-30	1.60	1-5	2×10^{-4}	35
221	E-30	1.60	1-5	2×10^{-4}	35
222	E-30	1.60	1-5	2×10^{-4}	35
223	E-30	1.60	1-5	2×10^{-4}	35
224	E-30	1.10	1-5	4×10^{-4}	34
225	E-30	1.10	1-5	4×10^{-4}	34
226	E-30	1.10	1-5	4×10^{-4}	34
227	E-30	1.10	1-5	4×10^{-4}	34
228	E-30	1.00	1-5	4×10^{-4}	34
229	E-30	1.00	1-5	4×10^{-4}	34
230	E-30	1.00	1-5	4×10^{-4}	34

(Table 16-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Surface active agent: Type	Surface active agent: Amount per one side (g/m^2)	Surface tension (mN/m)
208	1.10	1-10	5×10^{-3}	25
209	1.10	1-10	8×10^{-4}	30
210	1.10	1-10	1×10^{-3}	29
211	1.10	1-10	2×10^{-3}	27
212	1.10	1-10	8×10^{-4}	30
213	1.10	1-10	1×10^{-3}	29
214	1.10	1-10	2×10^{-3}	27
215	1.10	2-80	4×10^{-4}	30
216	1.10	2-80	7×10^{-4}	29
217	1.10	2-80	2×10^{-3}	27
218	1.10	2-80	4×10^{-3}	25
219	1.10	2-24	3×10^{-3}	25
220	1.10	2-24	3×10^{-3}	25
221	1.10	2-24	3×10^{-3}	25
222	1.10	2-24	3×10^{-3}	25
223	1.10	2-24	3×10^{-3}	25
224	1.10	2-81	6×10^{-4}	29
225	1.10	2-81	8×10^{-4}	28
226	1.10	2-81	4×10^{-3}	24
227	1.10	2-81	1×10^{-2}	21
228	1.10	2-33	2×10^{-3}	26
229	1.10	2-33	4×10^{-3}	24
230	1.10	2-33	2×10^{-2}	19

(Table 16-c)

Sample No.	Total gelatin amount/ one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Sensitizing dye Type	Sensitizing dye Amount (mg/mole AgX)	Remarks
208	2.70	10	-	-	Yes
209	3.20	5	Compound (2)	120	No
210	3.20	6	Compound (2)	120	No
211	3.20	8	Compound (2)	120	No
212	3.10	5	Compound (2)	120	No
213	3.10	6	Compound (2)	120	Yes
214	3.10	8	Compound (2)	120	Yes
215	2.70	5	Compound (2)	120	No
216	2.70	6	Compound (2)	120	Yes
217	2.70	8	Compound (2)	120	Yes
218	2.70	10	Compound (2)	120	Yes
219	2.70	10	-	-	Yes
220	2.70	10	Compound (44)	120	Yes
221	2.70	10	Compound (74)	120	Yes
222	2.70	10	Control (a)	120	Yes
223	2.70	10	Control (b)	120	Yes
224	2.20	5	Comound (2)	120	No
225	2.20	6	Comound (2)	120	Yes
226	2.20	10	Comound (2)	120	Yes
227	2.20	13	Comound (2)	120	Yes
228	2.10	8	Comound (2)	120	No
229	2.10	10	Comound (2)	120	No
230	2.10	15	Comound (2)	120	No

* Difference (between emulsion layer and protective layer)

Yes: Present invention No: Not the invention

Table 17

Sample No.	Coating trouble	Sensitivity	Granularity	Pressure desensitization	Abrasion blackening (g)	Drying characteristic
208	5	100	0.0023	0.19	25	5
209	4	85	0.0017	0.06	60	2
210	5	85	0.0017	0.06	60	2
211	5	85	0.0017	0.06	60	2
212	3	90	0.0018	0.07	57	3
213	4	90	0.0018	0.07	57	3
214	5	90	0.0018	0.07	58	3
215	1	120	0.0019	0.08	50	5
216	3	120	0.0019	0.08	50	5
217	4	120	0.0019	0.08	51	5
218	5	120	0.0019	0.08	52	5
219	5	75	0.0019	0.09	50	5
220	5	115	0.0019	0.08	52	5
221	5	120	0.0019	0.08	52	5
222	5	90	0.0019	0.09	52	5
223	5	95	0.0019	0.09	52	5
224	1	135	0.0020	0.09	45	5
225	3	135	0.0020	0.09	45	5
226	4	135	0.0020	0.09	46	5
227	5	135	0.0020	0.09	47	5
228	1	140	0.0023	0.10	41	5
229	2	140	0.0023	0.10	41	5
230	2	140	0.0023	0.10	42	5

Table 18

Sample No.	Total gelatin amount per one side (g/m^2)	Diff. in surface tension (dyn/cm) (mN/m)	Amount of sensitizing dye (mg/mol AgX)		Sensitivity 45 s processing	Sensitivity 90 s processing
211	3.20	8	Comp. (2)	120	85	105
214	3.10	8	Comp. (2)	120	90	110
218	2.70	10	Comp. (2)	120	120	135
219	2.70	10	-	-	75	90
226	2.20	10	Comp. (2)	120	135	145
229	2.10	10	Comp. (2)	120	140	150

Example 12

Here is described the preparation of emulsions E-31 to E-35 containing silver halide grains having a multi-layer structure. A 3.0N ammoniacal silver nitrate solution and a solution containing 2.0 mole % of potassium iodide and 98.0 mole % of potassium bromide were added in a gelatin solution according to a double jet method at 45 °C while keeping pAg = 11.0 and pH = 9.0. The addition rate was gradually accelerated with the growth of grains.

The resulting emulsion was found to be an octahedral monodispersed emulsion comprising grains

having an average grain size of 0.70 μm. Keeping pAg = 11.0 and pH = 9.0, an ammoniacal silver nitrate solution and a potassium bromide solution were further added according to a double jet method to form shells comprising silver bromide alone. An octahedral monodispersed emulsion comprising grains having an average grains size of 0.75 μm was obtained. This emulsion was designated E-31.

Following substantially the same procedures as those for E-31, provided, however, that the ratio of potassium iodide to potassium bromide was varied, the core size was varied so as to make the average silver iodide content after the formation of shells uniform, and the addition rate at an initial stage of mixing was controlled, there were prepared octahedral silver iodobromide emulsions containing 5 mole %, 10 mole %, 25 mole % and 40 mole % of silver iodide. Subsequent steps were the same as those for E-31 to prepare octahedral monodispersed emulsions comprising grains having an average grain size of 0.75 μm, which were respectively designated as E-32, E-33, E-34 and E-35. On E-29 and E-31 to E-35, chemical sensitization and coating were carried out in the same manner as in Example 1 to obtain samples No. 231 to No. 239. Profiles of the samples are shown in Table 19 (Table 19-a, -b, -c).

These samples were evaluated in the same manner as in Example 10 to obtain the results shown in Table 20.

As is clear from Table 20, the samples according to this invention have excellent in sensitivity, granularity, pressure desensitization, and abrasion blackening as a whole. It is also seen from the comparison with the conventional 90 second processing that the sensitivity is higher than the conventional system (samples No. 231 and No. 235), and yet the processing time can be shortened to 1/2 to provide twice the processing ability.

Table 19:

(Table 19-a)

Sample No.	Silver halide emulsion layer				
	Emulsion	Gelatin amount per one side (g/m^2)	Surface active agent Type	Surface active agent Amount per one side (g/m^2)	Surface tension (dyn/cm) (mN/m)
231	E-31	1.70	1-10	2×10^{-4}	35
232	E-33	1.70	1-10	2×10^{-4}	35
233	E-34	1.70	1-10	2×10^{-4}	35
234	E-35	1.70	1-10	2×10^{-4}	35
235	E-36	1.70	1-10	2×10^{-4}	35
236	E-36	1.70	1-10	2×10^{-4}	35
237	E-36	1.70	1-10	2×10^{-4}	35
238	E-36	1.70	1-10	2×10^{-4}	35
239	E-37	1.70	1-10	2×10^{-4}	35

(Table 19-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Protective layer: Surface active agent: Type	Protective layer: Surface active agent: Amount per one side (g/m^2)	Protective layer: Surface tension (dyn/cm) (mN/m)
231	1.00	1-10	5×10^{-3}	25
232	1.00	1-10	5×10^{-3}	25
233	1.00	1-10	5×10^{-3}	25
234	1.00	1-10	5×10^{-3}	25
235	1.00	1-10	5×10^{-3}	25
236	1.00	1-10	5×10^{-3}	25
237	1.00	1-10	5×10^{-3}	25
238	1.00	1-10	5×10^{-3}	25
239	1.00	1-10	5×10^{-3}	25

(Table 19-c)

Sample No.	Total gelatin amount/ one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Sensitizing dye Type	Sensitizing dye Amount (mg/mole AgX)	Remarks
231	2.70	10	-	-	Yes
232	2.70	10	Compound (2)	120	Yes
233	2.70	10	Compound (2)	120	Yes
234	2.70	10	Compound (2)	120	Yes
235	2.70	10	-	-	Yes
236	2.70	10	Compound (2)	120	Yes
237	2.70	10	Compound (74)	120	Yes
238	2.70	10	Control (c)	120	Yes
239	2.70	10	Compound (2)	120	Yes

* Difference (between emulsion layer and protective layer)

Yes: Present invention No: Not the invention

Table 20

Sample No.	Sensitivity		Granularity	Pressure desensitization	Abrasion blackening (g)
	45 s processing	90 s processing			
231	100	115	0.0023	0.19	25
232	115	130	0.0016	0.08	45
233	120	135	0.0016	0.09	47
234	130	145	0.0016	0.09	57
235	90	105	0.0016	0.09	60
236	135	150	0.0016	0.09	60
237	135	150	0.0016	0.09	58
238	100	115	0.0016	0.10	57
239	138	152	0.0016	0.10	62

Example 13

Formation of core grains was carried out by the same procedures as those for E-32 to E-35 to prepare octahedral silver iodobromide emulsions containing 5 mole %, 10 mole %, 25 mole % and 40 mole % of silver iodide. In the same procedure as that for E-31, except that shells were made to contain 1.0 mole % of potassium iodide, octahedral monodispersed emulsions comprising grains having an average grain size of 0.75 μm were prepared, which were respectively designated as E-36, E-37, E-38 and E-39.

Chemical sensitization and coating were carried out on these emulsions in the same manner as in Example 10 to obtain samples No. 240 to 247. Profiles of the samples are shown in Table 21 (Table 21-a, -b, -c).

These samples were evaluated in the same manner as in Example 10 to obtain the results shown in Table 22.

Table 21:

(Table 21-a)

Sample No.	Silver halide emulsion layer				
	Emulsion	Gelatin amount per one side (g/m^2)	Surface active agent Type	Surface active agent Amount per one side (g/m^2)	Surface tension (dyn/cm) (mN/m)
240	E-29	1.60	2-83	1×10^{-4}	35
241	E-36	1.60	2-83	1×10^{-4}	35
242	E-37	1.60	2-83	1×10^{-4}	35
243	E-38	1.60	2-83	1×10^{-4}	35
244	E-38	1.60	2-83	1×10^{-4}	35
245	E-38	1.60	2-83	1×10^{-4}	35
246	E-38	1.60	2-83	1×10^{-4}	35
247	E-39	1.60	2-83	1×10^{-4}	35

(Table 21-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Protective layer: Surface active agent: Type	Protective layer: Surface active agent: Amount per one side (g/m^2)	Protective layer: Surface tension (dyn/cm) (mN/m)
240	1.00	2-81	1×10^{-3}	27
241	1.00	2-81	1×10^{-3}	27
242	1.00	2-81	1×10^{-3}	27
243	1.00	2-81	1×10^{-3}	27
244	1.00	2-81	1×10^{-3}	27
245	1.00	2-81	1×10^{-3}	27
246	1.00	2-81	1×10^{-3}	27
247	1.00	2-81	1×10^{-3}	27

(Table 21-c)

Sample No.	Total gelatin amount/ one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Sensitizing dye Type	Sensitizing dye Amount (mg/mole AgX)	Remarks
240	2.60	8	-	-	Yes
241	2.60	8	Compound (44)	250	Yes
242	2.60	8	Compound (44)	250	Yes
243	2.60	8	-	-	Yes
244	2.60	8	Compound (44)	250	Yes
245	2.60	8	Compound (47)	250	Yes
246	2.60	8	Control (b)	250	No
247	2.60	8	Compound (44)	250	Yes

* Difference (between emulsion layer and protective layer)

Yes: Present invention No: Not the invention

Table 22

Sample No.	Sensitivity		Granularity	Pressure desensitization	Abrasion blackening (g)
	45 s processing	90 s processing			
240	103	118	0.0024	0.19	23
241	130	145	0.0017	0.08	42
242	140	155	0.0017	0.08	50
243	95	110	0.0017	0.09	55
244	145	160	0.0017	0.09	55
245	145	160	0.0017	0.09	54
246	105	120	0.0017	0.09	52
237	148	165	0.0017	0.09	58

As is clear from Table 22, the samples according to this invention have excellent in sensitivity,

granularity, pressure desensitization, and abrasion blackening as a whole, and it is also seen from a comparison with the conventional 90 second processing that the sensitivity is higher than the conventional system (samples No. 240 and No. 243), and yet the processing time can be shortened to 1/2 to provide twice the processing ability.

Example 14

A cubic monodispersed emulsion comprising silver iodobromide grains having an average grain size of 0.28 μm and containing 2.0 mole % of silver iodide was prepared by a double jet method while controlling the temperature to be 60 °C, pAg = 8.0 and pH = 2.0. Part of this emulsion was used as cores, and allowed to grow in the following manner. To the solutions containing the core grains and gelatin, an ammoniacal silver nitrate solution and a solution containing potassium iodide and potassium bromide were added at 40 °C, pAg 8.0 and pH 9.5 by a double jet method to form a first coat each containing 5 mole %, 10 mole %, 25 mole % or 40 mole % of silver iodide.

Each of the emulsions was treated in the same procedure as that for E-2, except that the pAg was 9.0, to form a second coat comprising silver bromide alone, thereby preparing core/shell emulsions comprising cubic monodispersed silver iodobromide grains having an average grain size of 0.65 μm, which were designated E-40, E-41, E-42 and E-43, respectively. All of these emulsions were made to have an average silver iodide content of 3.0 mole %.

On these monodispersed emulsions, chemical sensitization and coating were carried out in the same manner as in Example 10 to obtain samples No. 248 to No. 255. Profiles of the samples are shown in Table 23 (Table 23-a, -b, -c).

These samples were evaluated in the same manner as in Example 10 to obtain the results shown in Table 24.

Table 23:

(Table 23-a)

Sample No.	Silver halide emulsion layer				
	Emulsion	Gelatin amount per one side (g/m^2)	Surface active agent Type	Surface active agent Amount per one side (g/m^2)	Surface tension (dyn/cm) (mN/m)
248	E-29	1.50	2-82	1×10^{-4}	35
249	E-40	1.50	2-82	1×10^{-4}	35
250	E-41	1.50	2-82	1×10^{-4}	35
251	E-42	1.50	2-82	1×10^{-4}	35
252	E-42	1.50	2-82	1×10^{-4}	35
253	E-42	1.50	2-82	1×10^{-4}	35
254	E-42	1.50	2-82	1×10^{-4}	35
255	E-43	1.50	2-82	1×10^{-4}	35

(Table 23-b)

Sample No.	Protective layer: Gelatin amount per one side (g/m^2)	Protective layer: Surface active agent: Type	Protective layer: Surface active agent: Amount per one side (g/m^2)	Protective layer: Surface tension (dyn/cm) (mN/m)
248	1.10	2-82	4×10^{-3}	25
249	1.10	2-82	4×10^{-3}	25
250	1.10	2-82	4×10^{-3}	25
251	1.10	2-82	4×10^{-3}	25
252	1.10	2-82	4×10^{-3}	25
253	1.10	2-82	4×10^{-3}	25
254	1.10	2-82	4×10^{-3}	25
255	1.10	2-82	4×10^{-3}	25

(Table 23-c)

Sample No.	Total gelatin amount/ one side (g/m^2)	Diff.* in surface tension (dyn/cm) (mN/m)	Sensitizing dye Type	Sensitizing dye Amount (mg/mole AgX)	Remarks
248	2.60	10	-	-	Yes
249	2.60	10	Compound (74)	50	Yes
250	2.60	10	Compound (74)	50	Yes
251	2.60	10	-	-	Yes
252	2.60	10	Compound (74)	50	Yes
253	2.60	10	Compound (69)	50	Yes
254	2.60	10	Control (c)	50	Yes
255	2.60	10	Compound (74)	50	Yes

* Difference (between emulsion layer and protective layer)

Yes: Present invention No: Not the invention

Table 24

Sample No.	Sensitivity		Granularity	Pressure desensitization	Abrasion blackening (g)
	45 s processing	90 s processing			
248	103	118	0.0024	0.19	23
249	135	150	0.0014	0.06	45
250	150	165	0.0014	0.06	53
251	100	115	0.0014	0.06	55
252	155	170	0.0014	0.06	55
253	155	170	0.0014	0.06	55
254	110	125	0.0014	0.06	52
255	158	175	0.0014	0.07	57

As is clear from Table 24, the samples according to this invention have excellent sensitivity, granularity,

pressure desensitization, and abrasion blackening as a whole, and it is also seen by comparison with the conventional 90 second processing that the sensitivity is higher than the conventional system (samples No. 248 and No. 251), and yet the processing time can be shortened to 1/2 to provide twice the processing ability.

As described above, this invention provides a light-sensitive silver halide photographic material having excellent sensitivity, contrast, maximum density, fixing performance and drying characteristics even when an ultra rapid processing with a total processing time of 20 seconds to 60 seconds is carried out.

This invention also provides a light-sensitive silver halide photographic material being which has less problems during the coating stage, even with a small amount of gelatin, suffers less abrasion blackening or pressure desensitization, and also has excellent graininess.

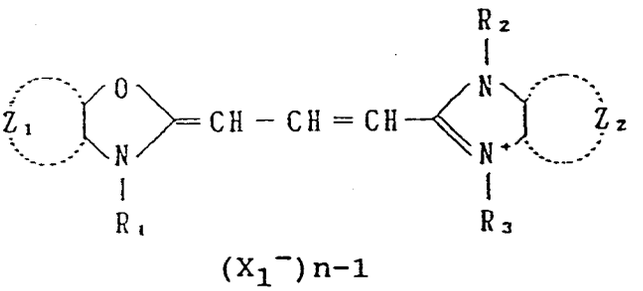
Claims

1. A light-sensitive silver halide photographic material which comprises photographic layers which have been applied under conditions such that the surface tension of a coating solution for forming an outermost layer is 6×10^{-3} N/m (6 dyn/cm) or more less than the surface tension of a solution for forming the layer adjacent to the outermost layer, which photographic material satisfies at least one of the conditions:

(a) the amount of gelatin contained in all of the layers on at least the side of the support having a light-sensitive silver halide emulsion layer and a hydrophilic colloid layer is from 2.20 to 3.10 g/m^2,

(b) the coating solution for forming the outermost layer and the solution for forming the layer adjacent thereto each have a viscosity of 20×10^{-3} Pas (20 cp) or less.

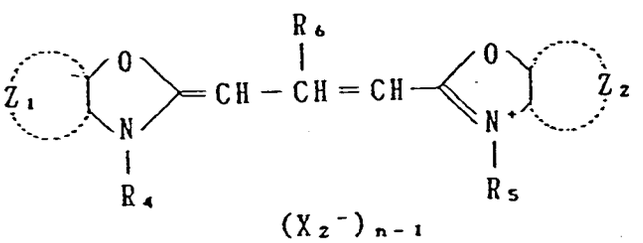
2. A photographic material according to claim 1, which comprises at least one silver halide emulsion layer containing at least one compound of formulae (I), (II) and (III):



$(X_1^-)_{n-1}$

wherein R_1, R_2 and R_3, which may be identical or different, each represents a substituted or unsubstituted alkyl group, alkenyl group or aryl group, at least one of R_1 and R_3 representing a sulfoalkyl group or a carboxyalkyl group; X_1^- represents an anion; Z_1 and Z_2, which may be identical or different, each represents a group of nonmetallic atoms which, together with the carbon atoms to which it is attached, forms a substituted or unsubstituted carbon ring; an n is 1 or 2, with the proviso that n is 1 when an intramolecular salt is formed;

Formula (II):

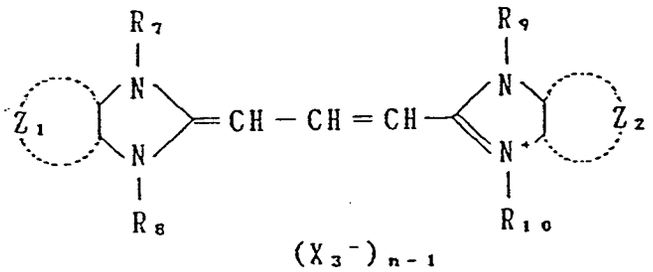


$(X_2^-)_{n-1}$

wherein R_4 and R_5, which may be identical or different, each represents a substituted or unsubstituted alkyl group, alkenyl group or aryl group, at least one of R_4 and R_5 representing a sulfoalkyl group or a carboxyalkyl group; R_6 represent a hydrogen atom, a lower alkyl group or an aryl group; X_2^-

represents an anion, Z_1 and Z_2, which may be identical or different, each represents a group of nonmetallic atoms which, together with the carbon atoms to which it is attached, forms a substituted or unsubstituted carbon ring; and n is 1 or 2, with the proviso that n is 1 when an intramolecular salt is formed;

Formula (III):



wherein R_7 and R_9, which may be identical or different, each represents a substituted or unsubstituted lower alkyl group; R_8 and R_{10}, which may be identical or different, each represents a lower alkyl group, a hydroxyalkyl group, a sulfoalkyl group or a carboxyalkyl group; X_3^- represents an anion, Z_1 and Z_2, which may be identical or different, each represents a group of nonmetallic atoms which, together with the carbon atoms to which it is attached, forms a substituted or unsubstituted carbon ring; and n is 1 or 2, with the proviso that n is 1 when an intramolecular salt is formed.

3. A photographic material according to claim 2, wherein X_1^- is a chloride ion, a bromide ion, an iodide ion, a thiocyanate ion, a sulfate ion, a perchlorate ion, a p-toluene sulfonate ion or an ethyl sulfate ion; and the substituted or unsubstituted carbon ring containing Z_1 and Z_2 in formula (I) is a substituted or unsubstituted benzene or naphthalene ring.

4. A photographic material according to claim 2, wherein R_6 is a methyl group, an ethyl group, a propyl group, a butyl group or a phenyl group; X_2^- is a chloride ion, a bromide ion, an iodide ion, a thiocyanate ion, a sulfate ion, a perchlorate ion, a p-toluene sulfonate ion or an ethyl sulfate ion; and the substituted or unsubstituted carbon ring containing Z_1 or Z_2 in formula (II) is a substituted or unsubstituted benzene or naphthalene ring.

5. A photographic material according to claim 2, wherein at least one of R_7 and R_9 is a methyl group, an ethyl group, a propyl group or a butyl group; at least one of R_8 and R_{10} is a methyl group, an ethyl group, a propyl group or a butyl group; X_3^- is a chloride ion, a bromide ion, an iodide ion, a thiocyanate ion, a sulfate ion, a perchlorate ion, a p-toluene sulfonate ion or an ethyl sulfate ion; and the substituted or unsubstituted carbon ring containing Z_1 or Z_2 in formula (III) is a substituted or unsubstituted benzene or naphthalene ring.

6. A photographic material according to any one of claims 2 to 5, wherein the total amount of compounds of formulae (I), (II) and (III) contained in the silver halide emulsion layer is from 10 mg to 900 mg per 1 mole of silver halide in the silver halide emulsion layer.

7. A photographic material according to any one of claims 2 to 6, wherein the silver halide emulsion layer comprises silver halide grains substantially comprising silver iodobromide and having a multi-layer structure, and the difference in average iodene content between two layers having uniform iodine distribution adjacent to each other in the multi-layers of the silver halide grains is 10 mole % or less.

8. A photographic material according to claim 7, wherein the inner nucleus and layers of the multi-layered silver halide grains comprise silver bromide, silver iodobromide or silver iodide.

9. A photographic material according to claim 7 or 8, wherein the outermost layer of the multi-layered silver halide grains comprises substantially silver bromide or silver iodobromide.

10. A photographic material according to any one of claims 1 to 9, wherein the outermost layer contains at least one surface active agent.

11. A photographic material according to any one of claims 1 to 10, wherein the difference in the viscosity between the coating solution for forming the outermost layer and the solution for forming the layer adjacent thereto is in the range of ± 2 x 10^{-3} Pas (2 cp).

12. A photographic material according to any one of claims 1 to 11, wherein the average grain size of silver halide emulsion grains contained in the light-sensitive silver halide colour photographic material is from 0.30 to 1.50 μm.

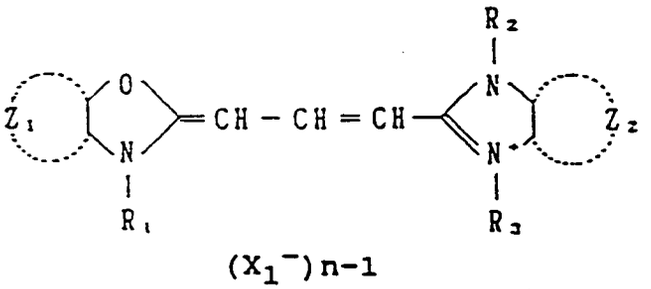
Patentansprüche

1. Lichtempfindliches photographisches Silberhalogenid-Aufzeichnungsmaterial, mit photographische Schichten, die unter solchen Bedingungen aufgetragen wurden, daß die Oberflächenspannung einer Beschichtungslösung zur Bildung einer äußersten Schicht 6 x 10^{-3} N/m (6 dyn/cm) oder mehr unter der Oberflächenspannung einer Lösung zur Bildung der der äußersten Schicht benachbarten Schicht beträgt, wobei das photographische Aufzeichnungsmaterial mindestens eine der Bedingungen erfüllt:

(a) die Menge an Gelatine in allen Schichten zumindest auf der Seite des Schichtträgers mit einer lichtempfindlichen Silberhalogenid-Emulsionsschicht und einer hydrophilen Kolloidschicht beträgt 2,20 bis 3,10 g/m^2,

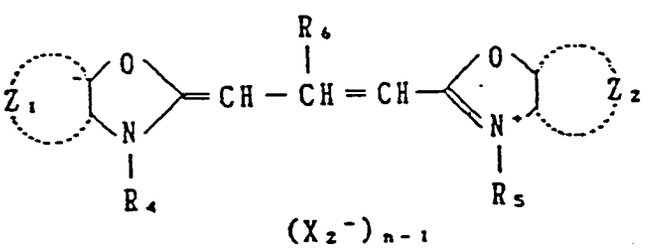
(b) die Beschichtungslösung zur Bildung der äußersten Schicht und die Lösung zur Bildung der Schicht, die zur äußersten benachbart ist, weisen jeweils eine Viskosität von 20 x 10^{-3} Pas (20 cp) oder weniger auf.

2. Photographisches Aufzeichnungsmaterial nach Anspruch 1, umfassend mindestens eine Silberhalogenid-Emulsionsschicht, die mindestens eine Verbindung der Formeln (I), (II) und (III) beinhaltet:



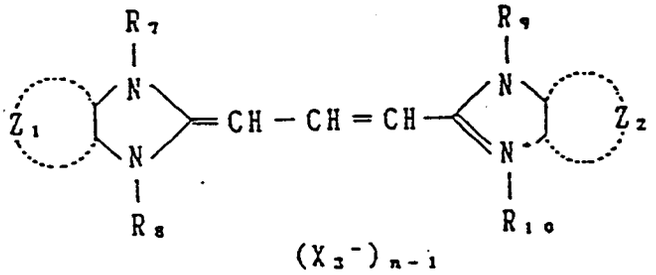
worin R_1, R_2 und R_3, die gleich oder unterschiedlich sein können, jeweils eine substituierte oder nicht substituierte Alkylgruppe, Alkenylgruppe oder Arylgruppe darstellen, wobei mindestens eine der Gruppen R_1 und R_3 eine Sulfoalkylgruppe oder eine Carboxyalkylgruppe darstellt; $X_1^{\ominus}$ ein Anion darstellt; Z_1 und Z_2, die gleich oder unterschiedlich sein können, jeweils für eine Gruppe von nichtmetallischen Atomen, die zusammen mit den Kohlenstoffatomen, an die sie gebunden ist, einen substituierten oder nicht substituierten Kohlenstoffring bildet, steht; n = 1 oder 2, wobei gilt, daß n = 1, wenn ein intramolekulares Salz gebildet wird;

Formel (II):



worin R_4 und R_5, die gleich oder unterschiedlich sein können, jeweils eine substituierte oder nicht substituierte Alkylgruppe, Alkenylgruppe oder Arylgruppe darstellen, wobei mindestens eine der Grup-

pen R_4 und R_5 eine Sulfoalkylgruppe oder eine Carboxyalkylgruppe darstellt; R_6 ein Wasserstoffatom, eine Niedrig-Alkylgruppe oder eine Arylgruppe darstellt; $X_2^{\ominus}$ ein Anion bedeutet; Z_1 und Z_2, die gleich oder unterschiedlich sein können, jeweils für eine Gruppe von nichtmetallischen Atomen, die zusammen mit den Kohlenstoffatomen, an die sie gebunden ist, einen substituierten oder nicht substituierten Kohlenstoffring bildet, steht; n = 1 oder 2, wobei gilt, daß n = 1, wenn ein intramolekulares Salz gebildet wird;
Formel (III):



worin R_7 und R_9, die gleich oder unterschiedlich sein können, jeweils eine substituierte oder nicht substituierte Niedrig-Alkylgruppe darstellen; R_8 und R_{10}, die gleich oder unterschiedlich sein können, jeweils eine Niedrig-Alkylgruppe, eine Hydroxyalkylgruppe, eine Sulfoalkylgruppe oder eine Carboxyalkylgruppe darstellen; $X_3^{\ominus}$ ein Anion bedeutet; Z_1 und Z_2, die gleich oder unterschiedlich sein können, jeweils für eine Gruppe von nichtmetallischen Atomen, die zusammen mit den Kohlenstoffatomen, an die sie gebunden ist, einen substituierten oder nicht substituierten Kohlenstoffring bildet, steht; n = 1 oder 2, wobei gilt, daß n = 1, wenn ein intramolekulares Salz gebildet wird.

3. Photographisches Aufzeichnungsmaterial nach Anspruch 2, worin $X_1^{\ominus}$ ein Chloridion, ein Bromidion, ein Jodidion, ein Thiocyanation, ein Sulfation, ein Perchloration, ein p-Toluolsulfonation oder ein Ethylsulfation darstellt; und worin der substituierte oder nicht substituierte Kohlenstoffring, der Z_1 und Z_2 in Formel (I) enthält, ein substituierter oder nicht substituierter Benzol- oder Naphtalinring ist.

4. Photographisches Aufzeichnungsmaterial nach Anspruch 2, worin R_6 eine Methylgruppe, eine Ethylgruppe, eine Propylgruppe, eine Butylgruppe oder eine Phenylgruppe darstellt; $X_2^{\ominus}$ ein Chloridion, ein Bromidion, ein Jodidion, ein Thiocyanation, ein Sulfation, ein Perchloration, ein p-Toluolsulfonation oder ein Ethylsulfation ist; und worin der substituierte oder nicht substituierte Kohlenstoffring, der in Z_1 oder Z_2 in Formel (II) enthält, ein substituierter oder nicht substituierter Benzol- oder Naphtalinring ist.

5. Photographisches Aufzeichnungsmaterial nach Anspruch 2, worin mindestens eine der Gruppen R_7 und R_9 eine Methylgruppe, eine Ethylgruppe, eine Propylgruppe oder eine Butylgruppe darstellt; worin mindestens eine der Gruppen R_8 und R_{10} eine Methylgruppe, eine Ethylgruppe, eine Propylgruppe oder eine Butylgruppe darstellt; $X_3^{\ominus}$ ein Chloridion, ein Bromidion, ein Jodidion, ein Thiocyanation, ein Sulfation, ein Perchloration, ein p-Toluolsulfonation oder ein Ethylsulfation ist; und worin der substituierte oder nicht substituierte Kohlenstoffring, der Z_1 oder Z_2 in Formel (III) enthält, ein substituierter oder nicht substituierter Benzol- oder Naphtalinring ist.

6. Photographisches Aufzeichnungsmaterial nach einem der Ansprüche 2 bis 5, worin die Gesamtmenge der Verbindungen der Formeln (I), (II) und (III), die in der Silberhalogenid-Emulsionsschicht enthalten sind, 10 mg bis 900 mg pro 1 Mol Silberhalogenid in der Silberhalogenid-Emulsionsschicht beträgt.

7. Photographisches Aufzeichnungsmaterial nach einem der Ansprüche 2 bis 6, worin die Silberhalogenid-Emulsionsschicht hauptsächlich Silberjodbromid enthaltende Silberhalogenid-Körnchen mit einer mehrlagigen Struktur enthält, wobei die Differenz des durchschnittlichen Jodgehalts der Silberhalogenid-Körnchen zwischen zwei in der Vielzahl der Schichten benachbart zueinander liegenden Schichten mit gleichmäßiger Jodverteilung 10 Mol% oder weniger beträgt.

8. Photographisches Aufzeichnungsmaterial nach Anspruch 7, worin der innere Kern und die Schichten der mehrlagigen Silberhalogenid-Körnchen Silberbromid, Silberjodbromid oder Silberjodid beinhalten.

9. Photographisches Aufzeichnungsmaterial nach Anspruch 7 oder 8, worin die äußerste Schicht der mehrlagigen Silberhalogenid-Körnchen hauptsächlich Silberbromid oder Silberjodbromid beinhaltet.

10. Photographisches Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 9, worin die äußerste Schicht mindestens ein oberflächenaktives Mittel enthält.

11. Photographisches Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 10, worin die Differenz in der Viskosität zwischen der Beschichtungslösung zur Bildung der äußersten Schicht und der Lösung zur Bildung der zur äußersten Schicht benachbart liegenden Schicht im Bereich von ± 2 x 10^{-3} Pas (2 cp) liegt.

12. Photographisches Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 11, worin die durchschnittliche Korngröße der Silberhalogenid-Emulsionskörnchen, die im lichtempfindlichen, farbphotographischen Silberhalogenid-Aufzeichnungsmaterial enthalten sind, 0,30 bis 1,50 µm beträgt.

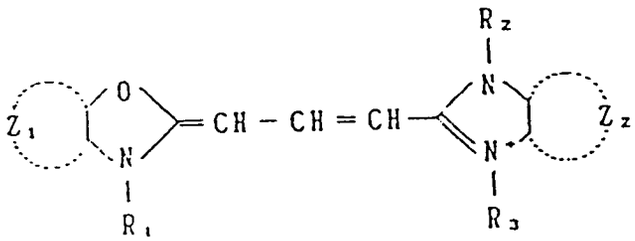
Revendications

1. Matière photographique à base d'halogénure d'argent sensible à la lumière qui comprend des couches photographiques qui ont été appliquées dans des conditions telles que la tension superficielle d'une solution de revêtement pour former une couche externe est au moins de 6 x 10^{-3} N/m (6 dyn/cm) moins que la tension superficielle d'une solution pour former la couche adjacente à la couche externe, laquelle matière photographique satisfait au moins une des conditions suivantes:

(a) la quantité de gélatine contenue dans toutes les couches, au moins du côté du support ayant une couche d'émulsion d'halogénure d'argent sensible à la lumière et une couche de colloïde hydrophile,est de 2,20 à 3,10 g/m^2,

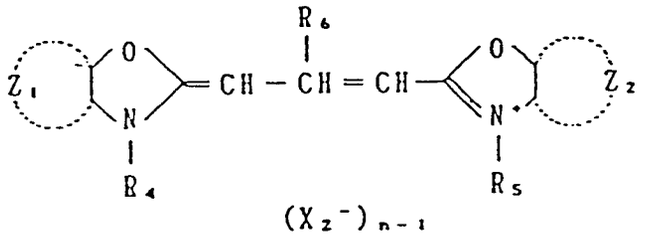
(b) la solution de revêtement pour former la couche externe et la solution pour former la couche qui y est adjacente ont l'une et l'autre une viscosité inférieure ou égale à 20 x 10^{-3} Pas (20 cp).

2. Matière photographique selon la revendication 1, qui comprend au moins une couche d'émulsion d'halogénure d'argent contenant au moins un composé de formules (I), (II) et (III):

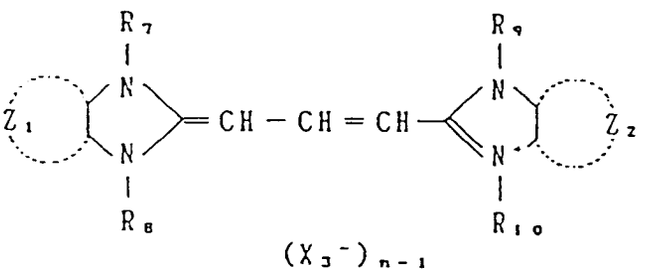


$(X_1^-)n-1$

dans laquelle R_1, R_2 et R_3, qui peuvent être identiques ou différents, représentent chacun un groupe alcoyle, un groupe alcényle ou un groupe aryle, substitué ou non substitué, au moins un des radicaux R_1 et R_3 représentant un groupe sulfoalcoyle ou un groupe carboxyalcoyle; X_1^- représente un anion; Z_1 et Z_2, qui peuvent être identiques ou différents, représentent chacun un groupe d'atomes non métalliques qui, avec les atomes de carbone auxquels il est lié, forme un noyau carboné substitué ou non substitué; n vaut 1 ou 2, sous réserve que n vaut 1 lorsqu'il s'agit d'un sel intramoléculaire ;
Formule (II):



dans laquelle R_4 et R_5, qui peuvent être identiques ou différents, représentent chacun un groupe alcoyle, un groupe alcényle ou un groupe aryle,substitué ou non substitué, au moins un des radicaux R_4 et R_5 représentant un groupe sulfoalcoyle ou un groupe carboxyalcoyle; R_6 représente un atome d'hydrogène, un groupe alcoyle inférieur ou un groupe aryle; X_2^- représente un anion, Z_1 et Z_2, qui peuvent être identiques ou différents, représentent chacun un groupe d'atomes non-métalliques qui, avec les atomes de carbone auxquels il est lié, forme un noyau carboné substitué ou non substitué; et n vaut 1 ou 2, sous réserve que n vaut 1 lorsqu'il s'agit d'un sel intramoléculaire ;
Formule (III):



dans laquelle R_7 et R_9, qui peuvent être identiques ou différents, représentent chacun un groupe alcoyle inférieur substitué ou non substitué; R_8 et R_{10}, qui peuvent être identiques ou différents, représentent chacun un groupe alcoyle inférieur, un groupe hydroxyalcoyle, un groupe sulfoalcoyle ou un groupe carboxyalcoyle; X_3^- représente un anion, Z_1 et Z_2, qui peuvent être identiques ou différents, représentent chacun un groupe d'atomes non métalliques qui, avec les atomes de carbone auxquels il est lié, forme un noyau carboné substitué ou non substitué; et n vaut 1 ou 2, sous réserve que n vaut 1 lorqu'il s'agit d'un sel intramoléculaire.

3. Matière photographique selon la revendication 2, dans laquelle X_1^- est un ion chlorure, un ion bromure, un ion iodure, un ion thiocyanate, un ion sulfate, un ion perchlorate, un ion p-toluènesulfonate ou un ion éthylsulfate; et le noyau carboné substitué ou non substitué contenant Z_1 et Z_2 dans la formule (I) est un noyau benzène ou naphtalène, substitué ou non substitué.

4. Matière photographique selon la revendication 2, dans laquelle R_6 est un groupe méthyle, un groupe éthyle, un groupe propyle, un groupe butyle ou un groupe phényle: X_2^- est un ion chlorure, un ion bromure, un ion iodure, un ion thiocyanate, un ion sulfate, un ion perchlorate, un ion p-toluènesulfonate ou un ion éthylsulfate; et le noyau carboné substitué ou non substitué contenant Z_1 ou Z_2 dans la formule (II) est un noyau benzène ou naphtalène,substitué ou non substitué.

5. Matière photographique selon la revendication 2, dans laquelle au moins un des radicaux R_7 et R_9 est un groupe méthyle, un groupe éthyle, un groupe propyle ou un groupe butyle; au moins un des radicaux R_8 et R_{10} est un groupe méthyle, un groupe éthyle, un groupe propyle ou un groupe butyle; X_3^- est un ion chlorure, un ion bromure, un ion iodure, un ion thiocyanate, un ion sulfate, un ion perchlorate, un ion p-toluènesulfonate ou un ion éthylsulfate; et le noyau carboné substitué ou non substitué contenant Z_1 ou Z_2 dans la formule (III) est un noyau benzène ou naphtalène substitué ou non substitué.

6. Matière photographique selon l'une quelconque des revendications 2 à 5, dans laquelle la quantité

totale de composés de formules (I), (II) et (III) contenue dans la couche d'émulsion d'halogénure d'argent est de 10 mg à 900 mg pour 1 mole d'halogénure d'argent dans la couche d'émulsion d'halogénure d'argent.

7. Matière photographique selon l'une quelconque des revendications 2 à 6, dans laquelle la couche d'émulsion d'halogénure d'argent comprend des grains d'halogénure d'argent comprenant essentiellement de l'iodobromure d'argent et ayant une structure multicouche, et la différence de teneur moyenne en iode entre deux couches adjacentes ayant une distribution d'iode uniforme, dans les multicouches des grains d'halogénure d'argent, est égale ou inférieure à 10 % molaire.

8. Matière photographique selon la revendication 7, dans laquelle le noyau interne et les couches des grains d'halogénure d'argent multicouches comprennent du bromure d'argent, de l'iodobromure d'argent ou de l'iodure d'argent.

9. Matière photographique selon la revendication 7 ou 8, dans laquelle la couche externe des grains d'halogénure d'argent multicouches comprend pour l'essentiel du bromure d'argent ou de l'iodobromure d'argent.

10. Matière photographique selon l'une quelconque des revendications 1 à 9, dans laquelle la couche externe contient au moins un agent tensio-actif.

11. Matière photographique selon l'une quelconque des revendications 1 à 10, dans laquelle la différence de viscosité entre la solution de revêtement pour former la couche externe et la solution pour former la couche qui y est adjacente est dans un intervalle de $\pm 2 \times 10^{-3}$ Pas (2 cp).

12. Matière photographique selon l'une quelconque des revendications 1 à 11, dans laquelle la granulométrie moyenne des grains d'émulsion d'halogénure d'argent contenus dans la matière photographique couleur à base d'halogénure d'argent sensible à la lumière est de 0,30 à 1,50 µm.