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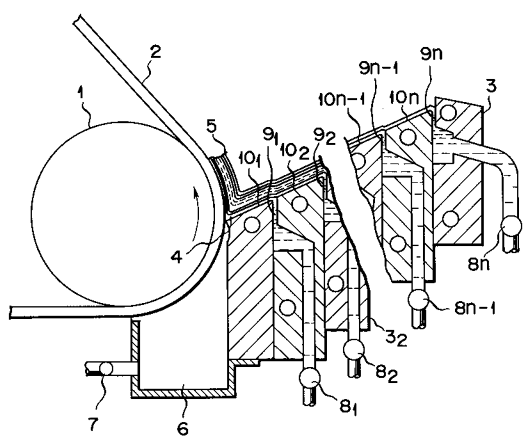
(54) **Silver halide color photographic light-sensitive material.**

(57) A silver halide color photographic light-sensitive material having, on a support, at least one of each of a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, and a red-sensitive silver halide emulsion layer. The light-sensitive material has at least 12 layers simultaneously coated on the support by one coating cycle, including the blue-, green-, and red-sensitive silver halide emulsion layers. The light-sensitive material contains at least one formalin scavenger in a total amount of 0.1 g/m^2 to 0.7 g/m^2 and at least one surfactant in a total amount of 0.1 g/m^2 to 0.7 g/m^2.



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The present invention relates to a silver halide color photographic light-sensitive material and, more particularly, to a silver halide color photographic light-sensitive material in which deterioration in photographic performance caused by formaldehyde gas is prevented and performance deterioration with time is suppressed.

Recently, the performance of a silver halide color photographic light-sensitive material has been remarkably advanced, and high quality can be obtained in performance such as color reproducibility, sharpness, and graininess. However, since the performance of a light-sensitive material is changed during storage before it is actually used after the manufacture, excellent performance of the material obtained immediately after the manufacture cannot be achieved.

The present inventor checked the actual use state of general-purpose color negative photographic materials in the market (Tokyo, Japan). As a result, it was found that about 40% of the entire color negative photographic materials have been stored for six months or more and about 10% of the materials have been stored for one year or more before they are used by general users after the manufacture. In addition, it is found that about 40% of the entire color negative photographic materials have been stored for two weeks or more and about 10% of the materials have been stored for one month or more before they are developed after the photographing. In these storage periods, performance deterioration is sometimes caused in the light-sensitive materials especially when they are stored at a high temperature or a high humidity.

In addition, furniture subjected to mothproofing with formalin have been widely spread in these days. If a photographic light-sensitive material loaded in a camera is left in such furniture, performance deterioration is caused in the light-sensitive material by formaldehyde gas.

As a method of preventing performance deterioration in a silver halide color photographic light-sensitive material caused by formaldehyde gas, the use of a formalin scavenger is disclosed in JP-A-58-10738 ("JP-A" means Unexamined Published Japanese Patent Application). JP-A-57-94752 discloses a technique of using a high-boiling organic solvent in combination with a two-equivalent magenta polymer coupler latex in place of a four-equivalent magenta polymer coupler latex. JP-A-61-73150 describes that deterioration in photographic performance caused by formalin gas can be prevented by using a combination of a two-equivalent magenta polymer coupler and a formalin scavenger.

However, although the performance deterioration caused by formalin gas can be prevented by adding the formalin scavenger to a light-sensitive material, a performance change in a light-sensitive material is increased when the material is stored at a high humidity.

It is, therefore, an object of the present invention to provide a silver halide color photographic light-sensitive material in which performance deterioration caused by formaldehyde gas is prevented and performance deterioration caused by long-term storage is suppressed.

In order to achieve the above object of the present invention, the present inventor has made extensive studies and found that performance deterioration with time can be suppressed by the manner of using a surfactant used in the manufacture of a light-sensitive material. In addition, the present inventor has unexpectedly found that the storage stability of a light-sensitive material is changed in accordance with the manner of coating coating layers in the manufacture of the light-sensitive material.

According to the present invention, there is provided a silver halide color photographic light-sensitive material having, on a support, at least one of each of a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, and a red-sensitive silver halide emulsion layer, wherein the light-sensitive material has at least 12 layers simultaneously coated on the support by one coating cycle, contains at least one formalin scavenger in an amount of 0.1 g/m^2 to 0.7 g/m^2, and contains a surfactant in an amount of 0.1 g/m^2 to 0.7 g/m^2.

In the preferred aspect of the present invention, the light-sensitive material of the present invention contains a surfactant represented by the following formula (A) in an amount of 0.1 g/m^2 to 0.6 g/m^2. Formula (A)

$$R\text{-}(L)_n SO_3^- M^+$$

where R represents an alkyl group, an aryl group, an aralkyl group, or an alkenyl group, with the total number of carbon atoms contained in R being 8 to 36, L represents a divalent linking group, n represents 0 or an integer of from 1 to 10, and M represents hydrogen or a cation.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a schematic side view showing a slide hopper type coating apparatus used in the present invention.

A formalin scavenger used in the present invention is a compound which reacts with formaldehyde gas, and includes a compound represented by the following formula (S):

Formula (S)

$$R_1-\underset{}{\overset{H}{\overset{|}{A}}}-R_2$$

where each of R_1 and R_2 independently represents a hydrogen atom, an alkyl group, an aryl group, an acyl group, an alkoxycarbamoyl group, a carbamoyl group, an imino group, or an amino group. The alkyl group and the aryl group may have substituent groups, and the alkyl group may be straight-chained or branched. R_1 and R_2 may form a ring or a fused ring. When R_1 and R_2 do not form a ring, at least one of R_1 and R_2 is an acyl group, a carbamoyl group, or an amino group.

A represents >CH- or >N-.

Preferable examples of a formalin scavenger represented by formula (S) are compounds represented by the following formulas (S-I), (S-II), (S-III), and (S-IV):

Formula (S-I)

$$(H_2N-\overset{O}{\overset{\|}{C}}-NH)_2-R_3$$

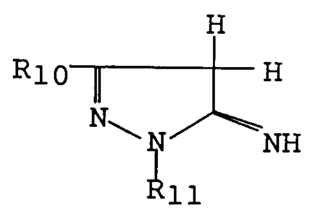
Formula (S-II)

$$R_4-NH-\overset{O}{\overset{\|}{C}}-\underset{\underset{R_5}{|}}{N}-R_6$$

Formula (S-III)

$$R_7-NH-R_8-NH-\overset{O}{\overset{\|}{C}}-R_9$$

Formula (S-IV)



In formulas (S-I) to (S-IV), R_3 represents a divalent alkyl group, each of R_4, R_5, and R_7 independently represents a hydrogen atom, an alkyl group, or

$$-\overset{O}{\overset{\|}{C}}-R'$$

(where R' represents a hydrogen atom), R_6 represents an alkyl group or an amino group, and R_9 represents an alkyl group which may have a substituent group. R_4 and R_6 may form a ring or a fused ring, and R_7 and R_9 may form a ring. When R_9 is a substituted alkyl group, examples of the substituent group are an amino group, a hydrocarbon group, or an -OR' group (where R' represents a hydrocarbon group). These amino and hydrocarbon groups may have substituent groups. R_8 represents a carbonyl group or a carboimidoyl group, and R_{10} represents a hydrogen atom, an alkyl group, a cyclohexyl group, a phenyl group, an aralkyl group, an alkoxyl group, an aryloxy group, a carbamoyl group, an alkoxycarbonyl group, or a cyano group. These groups may have substituting groups, if appropriate. R_{11} represents a hydrogen atom, an alkyl group, a cyclohexyl group, a phenyl group, an aralkyl group, a heterocyclic group, a benzoyl group, a sulfonalkyl group, a sulfonaryl group, a carboxyalkyl group, a carbazoyl group, or a thiocarbamoyl group.

When R_3, R_4, R_5, R_6, R_7, R_9 and R_{10} are alkyl groups, they preferably 1 to 8 carbon atoms.

Most preferable examples of a formalin scavenger represented by formula (S-I), (S-II), (S-III), or (S-IV) are listed in Table A to be presented later (SCV-1 to SCV-28), but the formalin scavenger is not limited to these examples.

Of these formalin scavengers, compounds SCV-1, SCV-2, SCV-5, SCV-6, SCV-7, and SCV-8 are commercially available, the other compounds such as SCV-7 to SCV-16 can be synthesized by methods described in, e.g., British Patent 717,287, U.S. Patents 2,731,472 and 3,187,004, and JP-A-58-79248, and compound SCV-19 can be synthesized by methods described in, e.g., Beilstein Handbuch der Organischer Chemie H98, (1921), Chemische der Berichte 54, B, PP. 1,802 to 1,833, PP. 2,441 to 2,477, (1921), and Bulletion of the Chemical Society of Japan, 39, PP. 1,559 to 1,567, PP. 1,734 to 1,738, (1966). Compound SCV-28 can be synthesized by a method described in German Patent 148,108.

The formalin scavengers for use in the present invention can be used in a combination of two or more types thereof.

The formalin scavenger for use in the present invention can be added to at least one layer of a silver halide color photographic light-sensitive material, e.g., protective layers, silver halide emulsion layers, interlayers, filter layers, an undercoating layer, an antihalation layer, and other auxiliary layers.

In order to add the formalin scavenger used in the present invention to these layers, the formalin scavenger may be directly added to a coating solution, or dissolved in a low-boiling organic solvent, such as water or alcohol, having no influence on a silver halide color photographic light-sensitive material, and then added to the solution. Alternatively, the formalin scavenger of the present invention may be dissolved in a high-boiling organic solvent and the resultant solution may be emulsion-dispersed in an aqueous solution, or may be impregnated in a two-equivalent magenta polymer latex and then added.

A coating amount of the formalin scavenger used in the present invention is 0.1 g/m^2 to 0.7 g/m^2. If the coating amount is less than 0.1 g/m^2, formaldehyde gas cannot be satisfactorily trapped. If the coating amount exceeds 0.7 g/m^2, a degree of performance deterioration caused by storage especially in a high-humidity atmosphere is increased. The coating amount of the formalin scavenger is more preferably 0.1 g/m^2 to 0.5 g/m^2, and most preferably, 0.1 g/m^2 to 0.3 g/m^2.

A surfactant used in the silver halide photographic light-sensitive material of the present invention includes various types of agents used in this field of art such as a coating aid, an antistatic agent, a slip properties modifier, an emulsion dispersant, an antiadhesion agent, and a photographic properties modifier (e.g., development acceleration, sensitization, and a high contrast treatment). Representative examples of the coating aid are described in, e.g., B.M. Deryagin, S.M. Levi, "Film Coating Theory", The Focal Press, 1964, PP. 159 to 164, U.S. Patents 4,242,444 and 4,547,459, JP-A-55-116799, and JP-A-60-209732. Representative compounds usable as the antistatic agent are described in Swiss Patent 506,093, British Patent 1,417,915, JP-A-57-146248, JP-A-58-208743, JP-A-61-143750, and Research Disclosure (RD) No. 23,815. Not a few of these compounds have an effect as an antiadhesion agent or a slip properties modifier. Representative compounds usable as the emulsion dispersant, in addition to the above surfactants used as coating aids, are described in JP-B-48-9979 ("JP-B" means Examined Published Japanese Patent Application), JP-A-50-66230, JP-A-51-129229, JP-A-53-138726, JP-A-54-99416, and JP-A-55-153933. A representative example of the photographic properties modifier is described in Kenichi Eda, "Studies on Surfactant 2, Application to Photographic Industry" (Sachi Shobo, 1963), PP. 384 to 391.

All of the above surfactants are representative examples, and commercially available surfactants can be added in accordance with various applications. Examples of the commercially available surfactant are described in Detergents & Emulsifiers (McCutcheon's Publications/Annual). Of these surfactants, however, a compound having power of decreasing the surface tension of water to 40 mN/m or less at 38°C when dissolved in water should be used. Examples of the surfactant compound will be listed in Table B to be presented later (A-1 to A-18, B-1 to B-6, C-1 to C-6, D-1 to D-18, and E-1 and E-2).

Of these surfactants, especially a surfactant represented by the following formula (A) has a large effect. The total amount of a surfactant represented by formula (A) is preferably 0.6 g/m^2 or less, and most preferably, 0.1 g/m^2 to 0.5 g/m^2. Formula (A)

$$R{+}L)_nSO_3\text{-}M^+$$

where R represents an alkyl group, an aryl group, an aralkyl group, or an alkenyl group, with the total number of carbon atoms contained in R being 8 to 36, L represents a divalent linking group, n represents 0 or an integer of from 1 to 10, and M represents hydrogen or a cation.

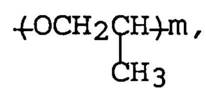
In formula (A), when R represents an alkyl group, the group may be straight-chained, cyclic, or branched and has 8 to 36, and more preferably, 12 to 24 carbon atoms. When R represents a substituted alkyl group, examples of the substituted group are a hydroxyl group, a carboxyl group, an amino group, a cyano group, a halogen atom, an alkoxycarbonyl group, and a carbonamide group. The alkyl group includes a group containing at least one of -O-, -S-, -CO-, $-CO_2-$, -CONR'-, $-SO_2$, $-SO_2NR'-$, -NR'CO-, and/or $-NR'SO_2-$ in a carbon chain (where R' represents a hydrogen atom, an alkyl group, or an aryl group).

When R represents an aryl group, the group preferably has a phenyl ring or a naphthyl ring and may have, on these rings, the groups enumerated above as the substituent groups usable when R represents the substituted alkyl group. More preferable examples of the aryl group are an alkylphenyl group and an alkylnaphthyl group, in which the total number of carbon atoms is 12 to 24 and which may have substituent groups.

When R represents an aralkyl group, the total number of carbon atoms is preferably 7 to 24. Examples are a benzyl group, a phenethyl group, and a 1-phenylethyl group.

When R represents an alkenyl group, the group may have a carbon-carbon double bond at any position and may be substituted by the groups enumerated above as the substituent groups usable when R represents the substituted alkyl group. Preferably, the group has 12 to 24 carbon atoms and one to five double bonds.

L represents a divalent linking group, and most preferably, -O-, -NH-, -CONH-, $\leftarrow OCH_2CH_2)m$, $\leftarrow OCH_2CH_2)mO-$,



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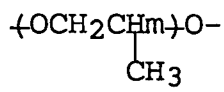


(where m represents an integer from 1 to 10, and most preferably, 1 to 5).

M represents a hydrogen atom or a cation, and preferably, H^+, K^+, Na^+, $1/2Mg^{2+}$, $1/2Ca^{2+}$, $1/2Ba^{2+}$, NH_4^+, Ag^+, and $N^+(R''_4)$ (wherein R'' represents an alkyl group which may be the same or different and has 4 to 32, and preferably, 4 to 16 carbon atoms.

Specific examples of a surfactant represented by formula (A) are listed in Table C to be presented later.

Conventionally, the silver halide color photographic light-sensitive material contains a large amount of surfactants because of a problem in coating techniques that the number of layers is large. That is, not only an amount of surfactants as coating aids is large, but also a large amount of surfactants is used as an emulsion dispersant for emulsion-dispersing couplers. To reduce the total amount of surfactants in the light-sensitive material without degrading its performance, it is desirable to reduce the number of times of coating by simultaneous multilayer coating, thereby reducing the amount of surfactants as coating aids.

The most preferable coating method as an aspect of the present invention is to complete a product by one multilayer simultaneous overlap coating cycle. As a result, a product with less performance change with time can be obtained. However, even by a separate coating method of two or more cycles, if one coating cycle of the method is a multilayer simultaneous overlap coating cycle of coating 12 or more layers and a plurality of layers coated at the same time include main emulsion layers (blue-, red- and green-sensitive emulsion layers), a target product having good storage stability can be obtained. For example, by separately coating an antihalation layer as the lowermost layer, two interlayers, two upper layers, i.e., first and second protective layers, and some of emulsion layers and performing multilayer simultaneous overlap coating for other 12 or more layers, a product with less performance deterioration with time can be completed.

In the present invention, it is preferred to complete a product by coating all layers including necessary silver halide emulsion layers by one multilayer simultaneous overlap coating cycle. In this case, or in a case wherein the first 12 or more layers are coated by the multilayer simultaneous overlap coating, it is preferred to use a coating solution having a viscosity of 15 cp to 100 cp in the lowermost layer adjacent to a support. That is, if the viscosity is less than 15 cp, color nonuniformity easily occurs in the simultaneous coating of

12 or more layers. If the viscosity exceeds 100 cp, coating properties become poor, and short of a solution easily occurs at two ends in the widthwise direction of a coating solution. The viscosity is preferably 20 to 70 cp, and more preferably, 20 to 60 cp.

In another aspect of the present invention, when separately coating two layers, i.e., an antihalation layer, for example, as the lowermost layer and an interlayer, a coating solution having a viscosity of 15 cp to 100 cp must be used in the lowermost layer adjacent to a support as described above in order to prevent color nonuniformity. However, this care is unnecessary in simultaneous coating of the subsequent 12 or more layers.

In the present invention, when completing a product by one multilayer simultaneous overlap coating cycle or performing multilayer simultaneous overlap coating for the first 12 or more layers, it is preferred to adjust the layers such that the viscosity of a coating solution of each of 10 or more layers, except for the uppermost layer, sequentially formed adjacent to each other on the lowermost layer is 30 cp or more and an arithmetic mean of the viscosities of the coating solutions of the 10 or more layers is 60 to 300 cp. That is, if the viscosity of the coating solution of each of the 10 or more layers, except for the uppermost layer, sequentially formed adjacent to each other on the lowermost layer is less than 30 cp, color nonuniformity easily occurs. If the viscosity exceeds 300 cp, it is difficult to supply the coating solution because the solution is not easily deaerated. The arithmetic mean of the viscosities of the coating solutions of the 10 or more layers is preferably 70 to 250 cp, and more preferably, 80 to 200 cp. In addition, the viscosity of the coating solution of the second layer adjacent to the lowermost layer is preferably larger than that of the lowermost layer. The viscosity of the second layer is more preferably 1.5 times or more, and most preferably, 1.8 to 5 times that of the lowermost layer. In view of the foregoing, the layers are coated by adjusting the arithmetic mean of the viscosities of the coating solutions of the 10 or more layers except for the lowermost and uppermost layers to be 60 to 300 cp.

When separately coating two layers, i.e., an antihalation layer, for example, as the lowermost layer and an interlayer, the viscosity of the coating solution of the lowermost layer and that of the second layer adjacent to the lowermost layer need not be made different from those of the subsequent upper coating solutions.

The viscosity of each coating solution can be adjusted to be a predetermined value by adding an aqueous solution of a well-known thickening agent. A typical example of the thickening agent is poly (sodium p-styrenesulfonate). In addition, a vinyl polymer having a sulfonic acid group, sulfate, a carboxyl group, or salts thereof on its side chain described in JP-A-63-11934 can also be used.

The viscosity is measured by using a B type viscometer (#BL: available from TOKYO KEIKI CO., LTD) at a shear rate of 29.8 mm/sec. (rotor No. 1, 30 rpm, temperature = 40 °C).

In the manufacturing method of the present invention, the coating amount of each layer is preferably 3 cc/m^2 or more. If the coating amount is smaller than this value, wavy nonuniformity is produced on the slide surface of a slide hopper (to be described later) to make it impossible to perform uniform multilayer coating on a support. The coating amount of each layer is more preferably 4 to 30 cc/m^2. When 12 or more layers are simultaneously coated while the coating amount of one layer is set to be 30 cc/m^2 or more, the coated photographic constituting layers easily cause color nonuniformity.

When completing a product by one multilayer simultaneous overlap coating or performing multilayer simultaneous overlap coating for the first 12 or more layers, the total coating amount of the lowermost layer and the 11 or more layers formed adjacent to the lowermost layer is preferably 250 cc/m^2 or less. When separately coating two layers, i.e., an antihalation layer, for example, as the lowermost layer and an interlayer, the total coating amount of the 12 or more layers including the lowermost layer is preferably 250 cc/m^2 or less. If the coating amount exceeds this upper limit, the coated photographic constituting layers easily cause color nonuniformity. In order to moderate drying conditions, the total coating amount is preferably 200 cc/m^2.

As a multilayer simultaneous coating apparatus for use in the present invention, an apparatus as described in JP-B-33-8977 is used. For example, a slide hopper coating apparatus capable of simultaneously coating 13 or more layers, like an n-layer simultaneous coating slide hopper apparatus as shown in Fig. 1, is used to supply predetermined coating solutions to 12 or more slits and coat the solutions so as to overlap each other while they are flowed on slide surfaces.

The slide hopper coating apparatus will be described below with reference to Fig. 1. A distal end 4 of a slide hopper liquid injecting device 3 is located close to a support 2 which moves while being supported by a back-up roller 1, with a predetermined interval therebetween, and a coating solution bridge (called a bead portion) 5 is formed in this portion, thereby coating solutions on the support 2. An interval between the support 2 and the distal end 4 is called a "bead interval". In order to stabilize the bead portion 5, a vacuum chamber 6 for evacuating a portion behind the bead is provided, and a vacuum pump 7 evacuates the chamber. A vacuum degree at that time is called a "bead back pressure".

The slide hopper liquid injecting device in the multilayer simultaneous coating apparatus will be described below. Coating solutions for n layers (assuming that the number of a plurality of layers is n) are supplied to the injecting device 3 by liquid supply pumps 8_l to 8_n, and thin coating solution films having a width corresponding to the full width of the support 2 are flowed from slits 9_l to 9_n onto slide surfaces 10_l to 10_n. The flowed thin coating solution films overlap each other from the upper portion of the device and simultaneously coated on the support as an n-layered overlapped coating solution films in the bead portion.

The apparatus is called a "slide hopper" because the respective coating solutions overlap each other on the slide surfaces.

The present invention can be applied to a multilayer simultaneous coating method of coating 12 or more layers. Although n = 12 to 20 layers can be generally, simultaneously coated, a multilayer simultaneous coating method of coating n = 13 to 18 layers can be preferably applied.

The coating rate in the color light-sensitive material manufacturing method of the present invention is 30 to 500 m/min as the moving speed of a support. The coating rate is preferably 60 to 300 m/min, and more preferably, 80 to 250 m/min.

The coated photographic constituting layers are dried by a conventional method. That is, the coated photographic constituting layers are cooled and solidified immediately after they are coated.

For this purpose, the layers are generally brought into contact with a low-temperature air at a dry-bulb temperature of -10°C to -20°C. After the coated films are cooled and solidified in this manner, drying is performed by air blow which is conventionally used. This drying using wind is generally performed by blowing an air at a dry-bulb temperature of 15°C to 45°C and a relative humidity of 10% to 50%, at an air flow of 10 to 40 $m^3/m^2 \cdot min$. This method is preferred because it can prevent an increase in fog caused by drying.

Although a necessary drying time depends on the wet coating amount and the drying conditions, it is normally 0.5 to 5 min. The coated films thus dried are preferably wetted by an air at a dry-bulb temperature of 20°C to 40°C and a relative humidity of 50% to 70%.

Representative examples of the support for the light-sensitive material of the present invention are those consisting of triacetylcellulose and polyethyleneterephthalate. The manufacturing method of the present invention is less adversely affected by undulations on the support than conventional manufacturing methods. Therefore, even if an undulation of a maximum of 5 µm is present, a color light-sensitive material having high surface quality can be coated at a high speed by the manufacturing method of the present invention. In a support having undulations, intervals between peaks of the undulations are preferably not 5 to 8 mm. An interval smaller or larger than this value is allowable. If the intervals between the peaks of the undulations are less than 4 mm or exceed 8 mm, the presence of undulations has almost no large influence on uniformity of coating.

The light-sensitive material of the present invention is constituted by at least 12 layers which are simultaneously coated and include silver halide emulsion layers, i.e., blue-sensitive layers, green-sensitive layers, and red-sensitive layers formed on a support.

In a multilayered silver halide color photographic light-sensitive material, unit light-sensitive layers are generally arranged such that red-, green-, and blue-sensitive layers are formed from a support side in the order named. However, this order may be reversed or a layer sensitive to one color may be sandwiched between layers sensitive to another color in accordance with the application.

JP-A-61-34541, JP-A-61-201245, JP-A-61-198236, and JP-A-62-160448 describe layer arrangements in which, in order to improve color reproducibility, the fourth or more light-sensitive layers are used in addition to conventional three types of blue-, green-, and red-sensitive layers. In this case, the fourth or more light-sensitive layers may be arranged in any position. The fourth or more light-sensitive layers may be either a single layer or constituted by a plurality of layers.

Non-light-sensitive layers such as various types of interlayers may be formed between the silver halide light-sensitive layers and as the uppermost layer and the lowermost layer.

The interlayer may contain, e.g., couplers and DIR compounds as described in JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037, and JP-A-61-20038 or a color mixing inhibitor which is normally used.

As a plurality of silver halide emulsion layers constituting each unit light-sensitive layer, a two-layered structure of high- and low-sensitivity emulsion layers can be preferably used as described in West German Patent 1,121,470 or British Patent 923,045. In this case, layers are preferably arranged such that the sensitivity is sequentially decreased toward a support, and a non-light-sensitive layer may be formed between the silver halide emulsion layers. In addition, as described in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541, and JP-A-62-206543, layers may be arranged such that a low-sensitivity emulsion layer is formed remotely from a support and a high-sensitivity layer is formed close to the support.

More specifically, layers may be arranged from the farthest side from a support in an order of low-sensitivity blue-sensitive layer (BL)/high-sensitivity blue-sensitive layer (BH)/high-sensitivity green-sensitive layer (GH)/low-sensitivity green-sensitive layer (GL)/high-sensitivity red-sensitive layer (RH)/low-sensitivity red-sensitive layer (RL), an order of BH/BL/GL/GH/RH/RL, or an order of BH/BL/GH/GL/RL/RH.

In addition, as described in JP-B-55-34932, layers may be arranged from the farthest side from a support in an order of blue-sensitive layer/GH/RH/GL/RL. Furthermore, as described in JP-A-56-25738 and JP-A-62-63936, layers may be arranged from the farthest side from a support in an order of blue-sensitive layer/GL/RL/GH/RH.

As described in JP-B-49-15495, three layers may be arranged such that a silver halide emulsion layer having the highest sensitivity is arranged as an upper layer, a silver halide emulsion layer having sensitivity lower than that of the upper layer is arranged as an interlayer, and a silver halide emulsion layer having sensitivity lower than that of the interlayer is arranged as a lower layer, i.e., three layers having different sensitivities may be arranged such that the sensitivity is sequentially decreased toward the support. When a layer structure is constituted by three layers having different sensitivities, these layers may be arranged in an order of medium-sensitivity emulsion layer/high-sensitivity emulsion layer/low-sensitivity emulsion layer from the farthest side from a support in a layer sensitive to one color as described in JP-A-59-202464.

In addition, an order of high-sensitivity emulsion layer/low-sensitivity emulsion layer/medium-sensitivity emulsion layer or low-sensitivity emulsion layer/medium-sensitivity emulsion layer/high-sensitivity emulsion layer may be adopted.

Furthermore, the arrangement can be changed as described above even when four or more layers are formed.

As described above, various layer types and arrangements can be selected in accordance with the application of the light-sensitive material.

In the light-sensitive material of the present invention, a preferable layer arrangement is as follows.

Layer 1 (Lowermost layer)	Antihalation layer
Layer 2	Interlayer
Layer 3	Low-sensitivity red-sensitive layer (RL)
Layer 4	High-sensitivity red-sensitive layer (RH)
Layer 5	Interlayer
Layer 6	Low-sensitivity green-sensitive layer (GL)
Layer 7	High-sensitivity green-sensitive layer (GH)
Layer 8	Interlayer
Layer 9	Low-sensitivity blue-sensitive layer (BL)
Layer 10	High-sensitivity blue-sensitive layer (BH)
Layer 11	1st protective layer
Layer 12 (Uppermost layer)	2nd protective layer

In the light-sensitive material of the present invention, the following layer arrangement is also very preferable.

Layer 1 (Lowermost layer)	Antihalation layer
Layer 2	Interlayer
Layer 3	Low-sensitivity red-sensitive layer (RL)
Layer 4	Medium-sensitivity red-sensitive layer (RM)
Layer 5	High-sensitivity red-sensitive layer (RH)
Layer 6	Interlayer
Layer 7	Low-sensitivity green-sensitive layer (GL)
Layer 8	Medium-sensitivity green-sensitive layer (GM)
Layer 9	High-sensitivity green-sensitive layer (GH)
Layer 10	Interlayer
Layer 11	Low-sensitivity blue-sensitive layer (BL)
Layer 12	Medium-sensitivity blue-sensitive layer (BM)
Layer 13	High-sensitivity blue-sensitive layer (BH)
Layer 14	1st protective layer
Layer 15 (Uppermost layer)	2nd protective layer

Although the total amount of a silver halide used in the present invention is not particularly limited, it is preferably 2.5 g/m^2 to 8 g/m^2, and more preferably, 2.5 g/m^2 to 6 g/m^2 in terms of a silver amount.

The density of silver with respect to a gelatin binder is not particularly limited. However, it is preferably set within the range of a silver amount (weight)/gelatin (weight) ratio of 0.01 to 5.0 in accordance with high-sensitivity emulsion layers, low-sensitivity emulsion layers, and applications.

A preferable silver halide contained in photographic emulsion layers of the photographic light-sensitive material of the present invention is silver iodobromide, silver iodochloride, or silver iodochlorobromide containing about 30 mol% or less of silver iodide. The most preferable silver halide is silver iodobromide or silver iodochlorobromide containing about 2 mol% to about 25 mol% of silver iodide.

Silver halide grains contained in the photographic emulsion may have regular crystals such as cubic, octahedral, or tetradecahedral crystals, irregular crystals such as spherical or tabular crystals, crystals having crystal defects such as twinned crystal faces, or composite shapes thereof.

A silver halide may consist of fine grains having a grain size of about 0.2 μm or less or large grains having a projected area diameter of about 10 μm, and an emulsion may be either a polydisperse or monodisperse emulsion.

A silver halide photographic emulsion which can be used in the light-sensitive material of the present invention can be prepared by methods described in, for example, Research Disclosure (RD) No. 17,643 (December, 1978), pp. 22 to 23, "I. Emulsion preparation and types" and RD No. 18,716 (November, 1979), page 648; P. Glafkides, "Chemie et Phisique Photographique", Paul Montel, 1967; G.F. Duffin, "Photographic Emulsion Chemistry", Focal Press, 1966; and V.L. Zelikman et al., "Making and Coating Photographic Emulsion", Focal Press, 1964.

Monodisperse emulsions described in, for example, U.S. Patents 3,574,628 and 3,655,394 and British Patent 1,413,748 are also preferred.

Also, tabular grains having an aspect ratio of about 5 or more can be used in the present invention. The tabular grains can be easily prepared by methods described in, e.g., Gutoff, "Photographic Science and Engineering", Vol. 14, PP. 248 to 257 (1970); U.S. Patents 4,434,226, 4,414,310, 4,433,048, and 4,439,520, and British Patent 2,112,157.

A crystal structure may be uniform, may have different halogen compositions in the interior and the surface layer thereof, or may be a layered structure. Alternatively, a silver halide having a different composition may be bonded by an epitaxial junction or a compound except for a silver halide such as silver rhodanide or zinc oxide may be bonded.

A mixture of grains having various types of crystal shapes may be used.

A silver halide emulsion layer is normally subjected to physical ripening, chemical ripening, and spectral sensitization steps before it is used. Additives for use in these steps are described in Research Disclosure Nos. 17,643 and 18,716, and they are summarized in the following table.

Well-known photographic additives usable in the present invention are also described in the above two RDs, and they are summarized in the following table.

	Additives	RD No.17643	RD No.18716
1.	Chemical sensitizers	page 23	page 648, right column
2.	Sensitivity increasing agents		do
3.	Spectral sensitizers, super sensitizers	pages 23-24	page 648, right column to page 649, right column
4.	Brighteners	page 24	
5.	Antifoggants and stabilizers	pages 24-25 pages 24-25	page 649, right column
6.	Light absorbent, filter dye, ultraviolet absorbents	pages 25-26	page 649, right column to page 650, left column
7.	Stain preventing agents	page 25, right column	page 650, left to right columns
8.	Dye image stabilizer	page 25	
9.	Hardening agents	page 26	page 651, left column
10.	Binder	page 26	do
11.	Plasticizers, lubricants	page 27	page 650, right column
12.	Coating aids, surface active agents	pages 26-27	do
13.	Antistatic agents	page 27	do

Various color couplers can be used in the present invention, and specific examples of these couplers are described in patents described in above-mentioned Research Disclosure (RD), No. 17643, VII-C to VII-G.

Preferred examples of a yellow coupler are described in, e.g., U.S. Patents 3,933,501, 4,022,620, 4,326,024, 4,401,752, and 4,248,961, JP-B-58-10739, British Patents 1,425,020 and 1,476,760, U.S. Patents 3,973,968, 4,314,023, and 4,511,649, and EP 249,473A.

Examples of a magenta coupler are preferably 5-pyrazolone and pyrazoloazole compounds, and more preferably, compounds described in, e.g., U.S. Patents 4,310,619 and 4,351,897, EP 73,636, U.S. Patents 3,061,432 and 3,725,067, Research Disclosure No. 24220 (June 1984), JP-A-60-33552, Research Disclosure No. 24230 (June 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, and JP-A-60-185951, U.S. Patents 4,500,630, 4,540,654, and 4,565,630, and WO No. 88/04795.

Examples of a cyan coupler are phenol and naphthol couplers, and preferably, those described in, e.g., U.S. Patents 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,343,011, and 4,327,173, EP Disclosure 3,329,729, EP 121,365A and 249,453A, U.S. Patents 3,446,622, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212, and 4,296,199, and JP-A-61-42658.

Preferable examples of a colored coupler for correcting additional, undesirable absorption of a colored dye are those described in Research Disclosure No. 17643, VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258, and British Patent 1,146,368. A coupler for correcting unnecessary absorption of a colored dye by a fluorescent dye released upon coupling described in U.S. Patent 4,774,181 or a coupler having a dye precursor group which can react with a developing agent to form a dye as a split-off group described in U.S. Patent 4,777,120 may be preferably used.

Preferable examples of a coupler capable of forming colored dyes having proper diffusibility are those described in U.S. Patent 4,366,237, British Patent 2,125,570, EP 96,570, and West German Patent Application (OLS) No. 3,234,533.

Typical examples of a polymerized dye-forming coupler are described in U.S. Patents 3,451,820, 4,080,221, 4,367,288, 4,409,320, and 4,576,910, and British Patent 2,102,173.

Couplers releasing a photographically useful residue upon coupling are preferably used in the present invention. DIR couplers, i.e., couplers releasing a development inhibitor are described in the patents cited in the above-described RD No. 17643, VII-F, RD No. 307105, VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, JP-A-63-37346, JP-A-63-37350, and U.S. Patents 4,248,962 and 4,782,012.

Preferable examples of a coupler for imagewise releasing a nucleating agent or a development accelerator are described in British Patents 2,097,140 and 2,131,188, JP-A-59-157638, and JP-A-59-170840.

Examples of a coupler which can be used in the light-sensitive material of the present invention are competing couplers described in, e.g., U.S. Patent 4,130,427; poly-equivalent couplers described in, e.g., U.S. Patents 4,283,472, 4,338,393, and 4,310,618; a DIR redox compound releasing coupler, a DIR coupler releasing coupler, a DIR coupler releasing redox compound, or a DIR redox releasing redox compound described in, e.g., JP-A-60-185950 and JP-A-62-24252; couplers releasing a dye which turns to a colored form after being released described in EP 173,302A and 313,308A; bleaching accelerator releasing couplers described in, e.g., RD. Nos. 11,449 and 24,241 and JP-A-61-201247; a legand releasing coupler described in, e.g., U.S. Patent 4,553,477; a coupler releasing a leuco dye described in JP-A-63-75747; and a coupler releasing a fluorescent dye described in U.S. Patent 4,774,181.

The couplers for use in this invention can be added to the light-sensitive material by various known dispersion methods.

Examples of a high-boiling organic solvent to be used in the oil-in-water dispersion method are described in U.S. Patent 2,322,027.

Examples of a high-boiling organic solvent to be used in the oil-in-water dispersion method and having a boiling point of 175°C or more at atmospheric pressure are phthalic esters (e.g., dibutylphthalate, dicyclohexylphthalate, di-2-ethylhexylphthalate, decylphthalate, bis(2,4-di-t-amylphenyl)phthalate, bis(2,4-di-t-amylphenyl)isophthalate, bis(1,1-di-ethylpropyl)phthalate), phosphates or phosphonates (e.g., triphenylphosphate, tricresylphosphate, 2-ethylhexyldiphenylphosphate, tricyclohexylphosphate, tri-2-ethylhexylphosphate, tridodecylphosphate, tributoxyethylphosphate, trichloropropylphosphate, and di-2-ethylhexylphenylphosphonate), benzoates (e.g., 2-ethylhexylbenzoate, dodecylbenzoate, and 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethyldodecaneamide, N,N-diethyllaurylamide, and N-tetradecylpyrrolidone), alcohols or phenols (e.g., isostearylalcohol and 2,4-di-tert-amylphenol), aliphatic carboxylates (e.g., bis(2-ethylhexyl)sebacate, dioctylazelate, glyceroltributylate, isostearyllactate, and trioctylcitrate), an aniline derivative (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), and hydrocarbons (e.g., paraffin, dodecylbenzene, and diisopropylnaphthalene). An organic solvent having a boiling point of about 30°C or more, and preferably, 50°C to about 160°C can be used as a co-solvent. Typical examples of the co-solvent are ethyl acetate, butyl acetate, ethyl propionate, methylethylketone, cyclohexanone, 2-ethoxyethylacetate, and dimethylformamide.

Steps and effects of a latex dispersion method and examples of an impregnating latex are described in, e.g., U.S. Patent 4,199,363 and West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

The present invention can be applied to various color light-sensitive materials. Examples of the material are a color negative film for a general purpose or a movie, a color reversal film for a slide or a television, color paper, a color positive film, and color reversal paper.

A support which can be suitably used in the present invention is described in, e.g., RD. No. 17643, page 28, RD. No. 18716, from the right column, page 647 to the left column, page 648.

In the light-sensitive material of the present invention, the sum total of film thicknesses of all hydrophilic colloidal layers (all the layers coated on the support, including emulsion layers, interlayers and protective layers) at the side having emulsion layers is preferably 22 μm or less, more preferably, 18 μm or less, and most preferably, 16 μm or less. A film swell speed $T_{1/2}$ is preferably 30 sec. or less, and more preferably, 20 sec. or less. The film thickness means a film thickness measured under moisture conditioning at a temperature of 25°C and a relative humidity of 55% (two days). The film swell speed $T_{1/2}$ can be measured in accordance with a known method in the art. For example, the film swell speed $T_{1/2}$ can be measured by using a swell meter described in Photographic Science & Engineering, A. Green et al., Vol. 19, No. 2, pp. 124 to 129. When 90% of a maximum swell film thickness reached by performing a treatment by using a color developing agent at 30°C for 3 min. and 15 sec. is defined as a saturated film thickness, $T_{1/2}$ is defined as a time required for reaching 1/2 of the saturated film thickness.

The film swell speed $T_{1/2}$ can be adjusted by adding a film hardening agent to gelatin as a binder or changing aging conditions after coating. A swell ratio is preferably 150% to 400%. The swell ratio is calculated from the maximum swell film thickness measured under the above conditions in accordance with a relation : (maximum swell film thickness - film thickness)/film thickness.

The color photographic light-sensitive material according to the present invention can be developed by conventional methods described in RD. No. 17643, pp. 28 and 29, and RD. No. 18716, the left to right columns, page 615.

When using the light-sensitive material of the present invention in the form of a roll, it is preferably housed in a cartridge. The most general cartridge is a 135-format patrone which is currently used. In addition, cartridges proposed in the following patents can be used. (Unexamined Published Japanese Utility Model Application No. 58-67329, JP-A-58-181035, JP-A-58-182634, Unexamined Published Japanese Utility Model Application No. 58-195236, U.S. Patent 4,221,479, Japanese Patent Application Nos. 63-57785, 63-183344, 63-325638, 1-21862, 1-25362, 1-30246, 1-20222, 1-21863, 1-37181, 1-33108, 1-85198, 1-172595, 1-172594, 1-172593, and U.S. Patents 4,846,418, 484,693, and 4,832,275.)

The present invention will be described in more detail below by way of its examples, but the present invention is not limited to these examples.

(Examples)

A multilayered color light-sensitive material was formed by simultaneously coating a plurality of layers having the following compositions on an undercoated triacetylcellulose film support.

(Compositions of light-sensitive layers)

A coating amount of a silver halide and colloidal silver is represented in units of g/m^2 of silver, and that of couplers, additives, and gelatin is represented in units of g/m^2. A coating amount of sensitizing dyes is represented by mols per mol of a silver halide in the same layer. Various compounds used will be listed in Table D (to be presented later).

Layer 1: Antihalation layer	
Black colloidal silver	0.20
Gelatin	1.30
UV-1	0.050
UV-2	0.050
UV-3	0.10
UV-4	0.10
Oil-1	0.10
Oil-2	0.10

Layer 2: Interlayer	
Gelatin	1.00

Layer 3: 1st red-sensitive emulsion layer

Silver iodobromide emulsion (AgI = 7.1 mol%, octahedral multiple structure grain, volume-equivalent sphere diameter = 0.4 μm, variation coefficient of equivalent sphere diameter = 15%)

coating silver amount	1.00
Gelatin	2.00
S-1	2.8×10^{-4}
S-2	2.0×10^{-4}
S-3	1.0×10^{-5}
Cp-1	0.40
Cp-2	0.040
Cp-3	0.020
Cp-4	2.0×10^{-3}
Oil-1	0.15
Oil-2	0.15

Layer 4: 2nd red-sensitive emulsion layer

Silver iodobromide emulsion (AgI = 7.7 mol%, octahedral multiple structure grain, volume-equivalent sphere diameter = 0.8 μm, variation coefficient of equivalent sphere diameter = 10%)

coating silver amount	1.20
Gelatin	0.80
S-1	2.0×10^{-4}
S-2	1.5×10^{-4}
S-3	8.0×10^{-6}
Cp-1	0.30
Cp-2	0.030
Cp-3	0.030
Cp-4	2.0×10^{-3}
Oil-1	0.12

Oil-2	0.12

Layer 5: 3rd red-sensitive emulsion layer

Silver iodobromide emulsion (AgI = 8.0 mol%, octahedral multiple structure grain, volume-equivalent sphere diameter = 1.1 μm, variation coefficient of equivalent sphere diameter = 13%) coating silver amount	1.00
Gelatin	1.50
S-1	1.5×10^{-4}
S-2	1.5×10^{-4}
S-3	8.0×10^{-6}
Cp-1	0.10
Cp-2	0.10
Oil-1	0.05
Oil-2	0.05

Layer 6: Interlayer	
Gelatin	0.70
Cpd-11	0.030
Oil-1	0.050

Layer 7: 1st green-sensitive emulsion layer

Silver iodobromide emulsion (AgI = 7.0 mol%, octahedral multiple structure grain, volume-equivalent sphere diameter = 0.4 μm, variation coefficient of equivalent sphere diameter = 15%) coating silver amount	1.10
Gelatin	2.50
S-4	2.4×10^{-4}
S-5	2.4×10^{-4}
S-6	1.2×10^{-4}
S-7	5.0×10^{-4}
Cp-5	0.15
Cp-6	0.10
Cp-7	0.030
Cp-8	0.020
Oil-1	0.30

Oil-2	0.30
Layer 8: 1st green-sensitive emulsion layer	
Silver iodobromide emulsion (AgI = 7.3 mol%, octahedral multiple structure grain, volume-equivalent sphere diameter = 0.7 μm, variation coefficient of equivalent sphere diameter = 9%) coating silver amount	1.10
Gelatin	0.80
S-4	2.0×10^{-4}
S-5	1.9×10^{-4}
S-6	1.1×10^{-4}
S-7	4.0×10^{-5}
Cp-5	0.10
Cp-6	0.070
Cp-7	0.030
Cp-8	0.025
Oil-1	0.20
Oil-2	0.20
Layer 9: 3rd green-sensitive emulsion layer	
Silver iodobromide emulsion (AgI = 7.5 mol%, thick plate aspect ratio = 2, volume-equivalent sphere diameter = 1.5 μm, variation coefficient of equivalent sphere diameter = 14%) coating silver amount	1.20
Gelatin	1.80
S-4	1.3×10^{-4}
S-5	1.3×10^{-4}
S-6	9.0×10^{-5}
S-7	3.0×10^{-5}
Cp-6	0.20
Cp-7	0.030
Oil-1	0.20
Oil-2	0.05

Layer 10: Yellow filter layer	
Yellow colloidal silver	0.080
Gelatin	1.20
Cpd-12	0.10
Oil-1	0.30

Layer 11: 1st blue-sensitive emulsion layer

Silver iodobromide emulsion (AgI = 6.5 mol%, octahedral multiple structure grain, volume-equivalent sphere diameter = 0.4 μm, variation coefficient of equivalent sphere diameter = 9%)

coating silver amount	0.20

Silver iodobromide emulsion (AgI = 7.0 mol%, octahedral multiple structure grain, volume-equivalent sphere diameter = 0.8 μm, variation coefficient of equivalent sphere diameter = 12%)

coating silver amount	0.45
Gelatin	1.75
S-7	1.0×10^{-4}
S-8	2.0×10^{-4}
Cp-9	0.45
Cp-10	0.50
Oil-1	0.20
Oil-2	0.10

Layer 12: 2nd blue-sensitive emulsion layer

Silver iodobromide emulsion (AgI = 9.7 mol%, thick plate aspect ratio = 2, volume-equivalent sphere diameter = 1.6 μm, variation coefficient of equivalent sphere diameter 12%)

coating silver amount	1.10
Gelatin	1.20
S-7	1.0×10^{-4}
S-8	1.0×10^{-4}
Cp-9	0.25
Oil-1	0.060
Oil-2	0.030

Layer 13: 1st protective layer	
Fine grain silver iodobromide emulsion (AgI = 2.0 mol%, average grain size = 0.08 μm)	
coating silver amount	0.40
Gelatin	1.30
UV-1	0.050
UV-2	0.050
UV-3	0.10
UV-4	0.10
UV-5	0.030
Oil-1	0.10
Oil-2	0.10

Layer 14: 2nd protective layer	
Gelatin	0.50
Polymethylmethacrylate grains (diameter = 1.5 μm)	0.20
B-11	0.030

In addition to the above components, film hardeners H-11 and H-12, compounds Cpd-15 and Cpd-16 as antiseptic agents, a stabilizer Cpd-17, and antifoggants Cpd-18 and Cpd-19 were added to the respective layers.

Samples 101 to 106 were formed by changing the amounts of the surfactants and the formalin scavengers as shown in Table 1.

In addition, in the sample 106, the 14 layers were not simultaneously formed by multilayer coating, but after the layer 6 was coated and dried, the layers 7 to 14 were subsequently coated, thereby forming a sample 107.

Similar to an ordinary 135 color negative film, each of the samples 101 to 107 was cut and loaded in an ISO-400 color negative film patrone, and the following tests were conducted.

Storage conditions

a) Temperature = 40 ° C, relative humidity = 80%, 14 days

b) Temperature = 20 ° C, relative humidity = 60%, 14 days

c) In newly purchased cabinet of general household, 14 days

After stored under the above conditions, each sample was used to photograph a person with a gray plate having a reflecting ratio of 18%, at 11 a.m. on a fine day in summer by using a camera cardiahyte available from Fuji Photo Film Co., Ltd. Each photographed sample was stored at a temperature of 30 ° C and a relative humidity of 60% for seven days and developed under the processing conditions (A). Subsequently, each processed sample was printed on Fuji Color Paper Super HG using an auto printer FAP 3500 available from Fuji Photo Film Co., Ltd. The printing conditions of the auto printer were set such that the color balance of each sample stored under the storage conditions (b) was optimized.

Table 1

Sample No.	Surfactant		Formalin scavenger		Coating method	Remarks
	Type	Amount [g/m^2]	Type	Amount [g/m^2]		
101	A-1 A-6 A-10 C-3	0.05 0.05 0.2 0.01	SCV-8 SCV-19	0.15 0.15	14-layer simul-taneous coating	Present Invention
102	A-1 A-6 A-10 C-3	0.05 0.05 0.2 0.01	-	0	ditto	Comparative Example
103	A-1 A-6 A-10 C-3	0.05 0.05 0.2 0.01	SCV-8 SCV-19	0.3 0.3	ditto	Present Invention
104	A-1 A-6 A-10 C-3	0.05 0.05 0.2 0.01	SCV-8 SCV-19	0.45 0.45	ditto	Comparative Example

(Continued)

Table 1

Sample No.	Surfactant Type	Surfactant Amount [g/m2]	Formalin scavenger Type	Formalin scavenger Amount [g/m2]	Coating method	Remarks
105	A-1 A-6 A-10 C-3	0.2 0.2 0.2 0.01	SCV-8 SCV-19	0.15 0.15	ditto	Present Invention
106	A-1 A-6 A-10 C-3	0.3 0.4 0.2 0.01	SCV-8 SCV-19	0.15 0.15	ditto	Comparative Example
107	A-1 A-6 A-10 C-3	0.3 0.4 0.2 0.01	SCV-8 SCV-19	0.15 0.15	Two-time separate coating of from layer 1 to layer 6 and from layer 7 to layer 12	Comparative Example

The color density in a portion of the gray plate of each print obtained by the samples 101 to 107 was measured by a Macbeth densitometer, thereby evaluating shifts in color balance caused by the storage conditions of the respective samples. The evaluation results are represented by the print densities of the respective samples stored under the storage conditions (a) and (c) with respect to those stored under the storage conditions (b), and summarized in Table 2.

As is apparent from Table 2, the sample 102 could not be practically used because color unbalance was caused by an influence of formalin gas generated by furniture during a storage period of only two weeks. In each of the samples of the present invention in which the amount of surfactants was reduced by simultaneous overlap coating and the amount of formalin scavengers was also reduced, a color unbalance was small to realize a high storage stability even under the storage conditions of a high temperature and a high humidity.

The effects of the present invention can be similarly achieved by conducting the tests by changing the processing conditions of negative films to (B).

Table 2

Sample No.	Surfactant amount [g/m^2]	Formalin scavenger amount [g/m^2]	Coating method	Shift in color balance*	
				Storage conditions a)	Storage conditions c)
101 (Presnet Invention)	0.31	0.3	14-layer simultaneous coating	0.05 YR shift	0.02 G shift
102 (Comparison Example)	0.31	0	ditto	0.03 YR shift	$\underline{0.32}$ CG shift
103 (Present Invention)	0.31	0.6	ditto	0.05 YR shift	0.01 YR shift
104 (Comparison Example)	0.31	0.9	ditto	$\underline{0.12}$ YR shift	0.01 YR shift
105 (Present Invention)	0.61	0.3	ditto	0.06 YR shift	0.01 YR shift
106 (Comparison Example)	0.91	0.3	ditto	$\underline{0.15}$ YR shift	0.01 YR shift
107 (Comparison Example)	0.91	0.3	Two-time coating (6 layers + 8 layers)	$\underline{0.18}$ YR shift	0.03 MR shift

* Shift in color balance is represented by change in print density with respect to storage conditions (b).

B shift = shift toward blue
G shift = shift toward green
R shift = shift toward red

Y shift = shift toward yellow
M shift = shift toward magenta
C shift = shift toward cyan

(Numerals with an under line indicate shift in color balance out of an allowable range)

Processing Method (A)		
Process	Time	Temperature
Color development	3 min. 15 sec.	38°C
Bleaching	6 min. 30 sec.	38°C
Washing	2 min. 10 sec.	24°C
Fixing	4 min. 20 sec.	38°C
Washing (1)	1 min. 05 sec.	24°C
Washing (2)	1 min. 00 sec.	24°C
Stabilization	1 min. 05 sec.	38°C
Drying	4 min. 20 sec.	55°C

The compositions of the processing solutions will be presented below.

Color developing solution:	(g)
Diethylenetriaminepentaacetate	1.0
1-hydroxyethylidene-1,1-diphosphonic acid	3.0
Sodium sulfite	4.0
Potassium carbonate	30.0
Potassium bromide	1.4
Potassium iodide	1.5 mg
Hydroxylamine sulfate	2.4
4-[N-ethyl-N-β-hydroxylethylamino] -2-methylaniline sulfate	4.5
Water to make	1.0 ℓ
pH	10.05

Bleaching solution:	(g)
Ferric Sodium ethylenediaminetetraacetate trihydrate	100.0
Disodium ethylenediaminetetraacetate	10.0
Ammonium bromide	140.0
Ammonium nitrate	30.0
Ammonia water (27%)	6.5 mℓ
Water to make	1.0 ℓ
pH	6.0

Fixing solution:	(g)
Disodium ethylenediaminetetraacetate	0.5
Sodium sulfite	7.0
Sodium bisulfite	5.0
Ammonium thiosulfate aqueous solution (70%)	170.0 mℓ
Water to make	1.0 ℓ
pH	6.7

Stabilizing solution:	(g)
Formalin (37%)	2.0 mℓ
Polyoxyethylene-p-monononylphenylether (average polymerization degree = 10)	0.3
Disodium ethylenediaminetetraacetate	0.05
Water to make	1.0 ℓ
pH	5.0 - 8.0

Processing Method (B)

Process	Time	Temperature	*Replenishing amount	Tank volume
Color development	3 min. 15 sec.	37.8°C	25 mℓ	10 ℓ
Bleaching	45 sec.	38°C	5 mℓ	4 ℓ
Bleach-fixing (1)	45 sec.	38°C	-	4 ℓ
Bleach-fixing (2)	45 sec.	38°C	30 mℓ	4 ℓ
Washing (1)	20 sec.	38°C	-	2 ℓ
Washing (2)	20 sec.	38°C	30 mℓ	2 ℓ
Stabilization	20 sec.	38°C	20 mℓ	2 ℓ
Drying	1 min.	55°C		

* A replenishing amount per meter of a 35-mm wide sample

Each of the bleach-fixing and washing steps was performed by a counter flow system piping from (2) to (1), and all of an overflow solution of the bleaching solution was supplied to the bleach-fixing step (2).

In the above processing, an amount of the bleach-fixing solution carried to the washing step was 2 mℓ per meter of a 35-mm wide light-sensitive material.

Color developing solution:	Mother solution (g)	Replenishment solution (g)
Diethylenetriaminepentaacetate	5.0	6.0
Sodium sulfite	4.0	4.4
Potassium carbonate	30.0	37.0
Potassium bromide	1.3	0.5
Potassium iodide	1.2 mg	-
Hydroxylamine sulfate	2.0	3.6
4-[N-ethyl-N-β-hydroxylethylamino] -2-methylaniline sulfate	4.7	6.2
Water to make	1.0 ℓ	1.0 ℓ
pH	10.00	10.15

Bleaching solution:	Mother solution (g)	Replenishment solution (g)
Ferric ammonium 1,3-diaminopropanetetraacetate monohydrate	144.0	206.0
1,3-diaminopropanetetraacetate	2.8	4.0
Ammonium bromide	84.0	120.0
Ammonium nitrate	17.5	25.0
Ammonia water (27%)	10.0	1.8
Acetic acid (98%)	51.1	73.0
Water to make	1.0 ℓ	1.0 ℓ
pH	4.3	3.4

Bleach-fixing solution:	Mother solution (g)	Replenishment solution (g)
Ferric ammonium ethylenediaminetetraacetate dihydrate	50.0	-
Disodium ethylenediaminetetraacetate	5.0	25.0
Ammonium sulfite	12.0	20.0
Ammonium thiosulfate aqueous solution (700 g/ℓ)	290.0 mℓ	320.0 mℓ
Ammonia water	6.0 mℓ	15.0 mℓ
Water to make	1.0 ℓ	1.0 ℓ
pH	6.8	8.0

Washing Solution: Common for mother and replenishment solutions

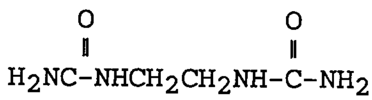
Tap water was supplied to a mixed-bed column filled with an H type strongly acidic cation exchange resin (Amberlite IR-120B: available from Rohm & House Co.) and an OH type strongly basic anion exchange resin (Amberlite IR-400) to set the concentrations of calcium and magnesium to be 3 mg/ℓ or less. Subsequently, 20 mg/ℓ of sodium isocyanuric acid dichloride and 150 mg/ℓ of sodium sulfate were added. The pH of the solution fell within the range of 6.5 to 7.5.

Stabilizing solution:	Common for mother and replenishment solutions (g)
Formalin (37%)	1.2 mℓ
Surfactant $[C_{10}H_{21}\text{-O}\text{-}(CH_2CH_2O)_{10}H]$	0.4
Ethyleneglycol	1.0
Water to make	1.0 ℓ
pH	5.0 - 7.0

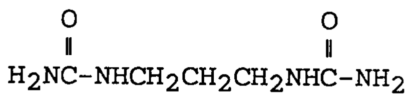
As has been described above, the arrangement of the present invention can prevent performance deterioration caused by formalin gas and improve storage stability at a high temperature and a high humidity.

Table A

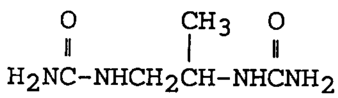
(SCV-1)



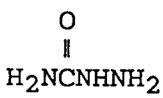
(SCV-2)



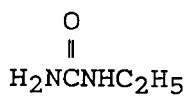
(SCV-3)



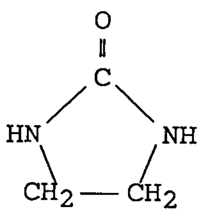
(SCV-4)



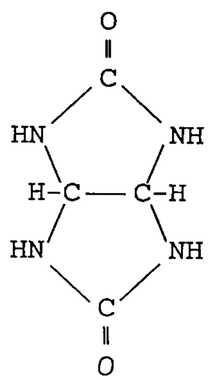
(SCV-5)



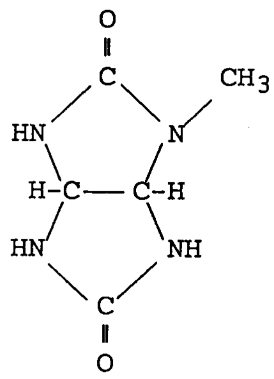
(SCV-6)



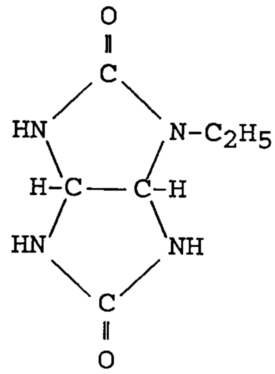
(SCV-7)



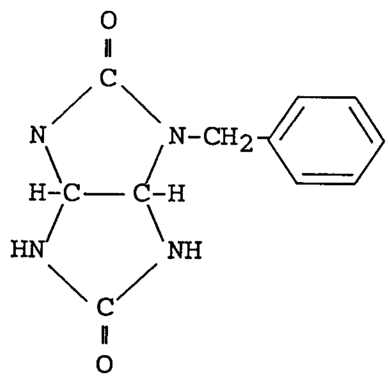
(SCV-8)



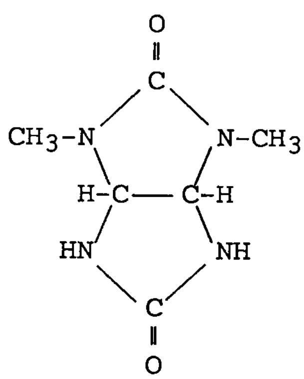
(SCV-9)



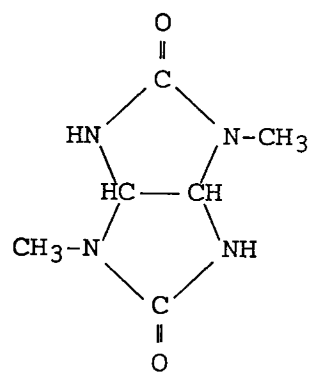
(SCV-10)



(SCV-11)



(SCV-12)



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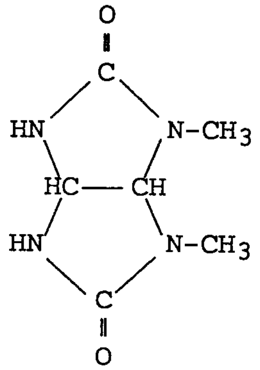

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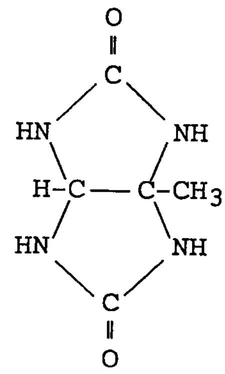
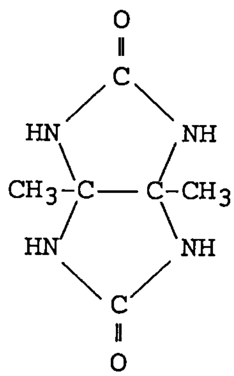
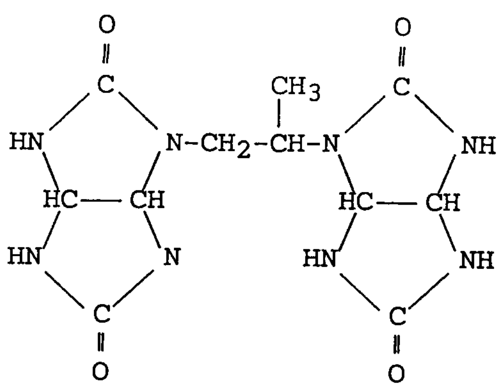


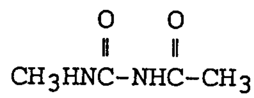
(SCV-15)



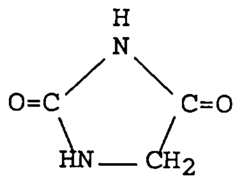
(SCV-16)



(SCV-17)



(SVC-18)



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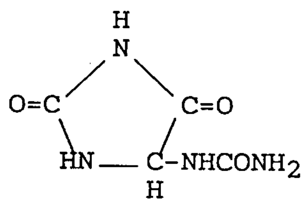
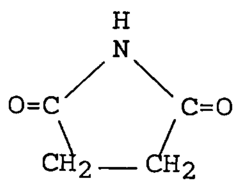
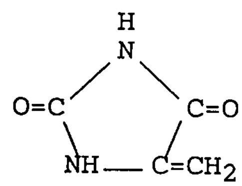


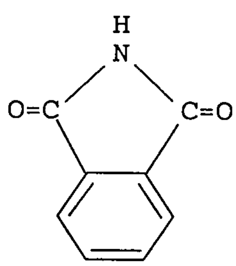
(SVC-20)



(SVC-21)



(SVC-22)



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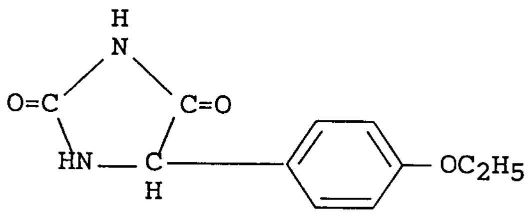
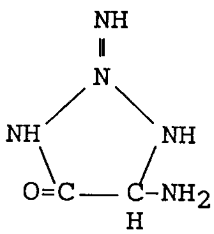
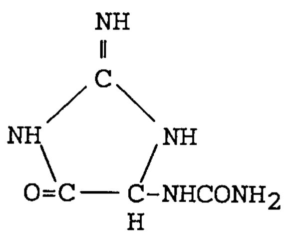


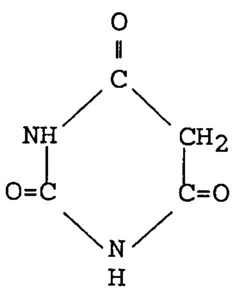
(SVC-24)



(SVC-25)



(SVC-26)



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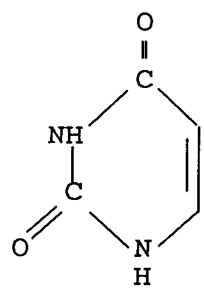

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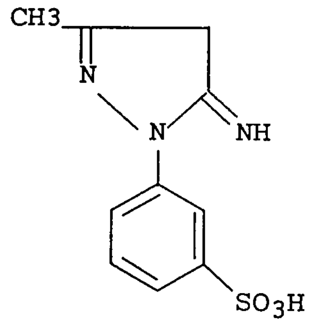
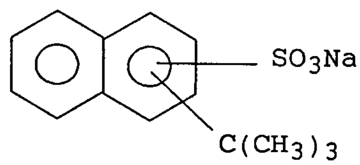


Table B

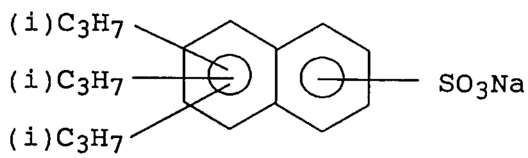
A-1

$$\begin{array}{l} NaO_3S-CH\cdot COOCH_2CH(C_2H_5)C_4H_9 \\ \qquad\quad\ \ | \\ \qquad\quad\ CH_2COOCH_2CH(C_2H_5)C_4H_9 \end{array}$$

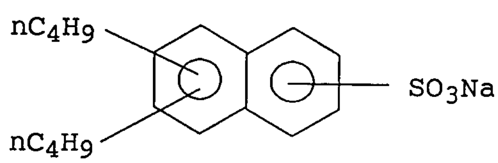
A-2



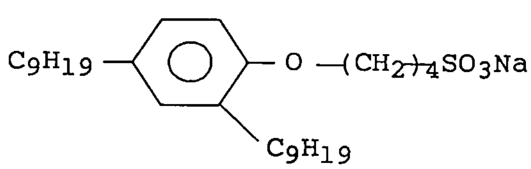
A-3



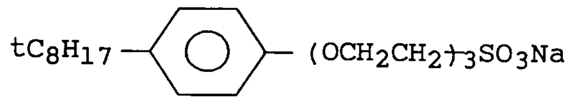
A-4



A-5



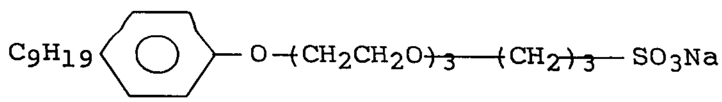
A-6



A-7

$CH_3(CH_2)_{10}CH=CHCH_2SO_3Na$

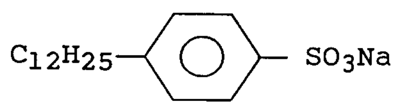
A-8



A-9

$$C_{17}H_{33}CO\underset{\overset{|}{CH_3}}{N}-CH_2-CH_2-SO_3Na$$

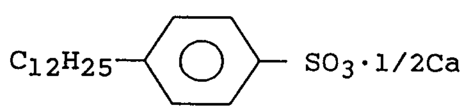
A-10



A-11

$C_{12}H_{25}OSO_3Na$

A-12



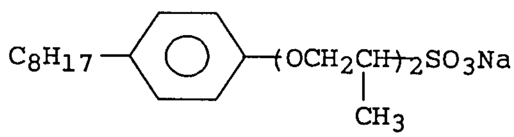
A-13

$$\begin{array}{l} NaO_3S\text{-}CHCOO(CH_2CH_2O)C_6H_{13} \\ \qquad\quad | \\ \qquad\quad CH_2COO(CH_2CH_2O)C_6H_{13} \end{array}$$

A-14

$$\begin{array}{l} \qquad\quad\; CH_2COOC_5H_{11} \\ \qquad\quad\; | \\ \quad HO\text{-}C\text{-}COOC_5H_{11} \\ \qquad\quad\; | \\ NaO_3S\text{-}CH\text{-}COOC_5H_{11} \end{array}$$

A-15



A-16

$$\begin{array}{l} \qquad\quad CH_2COOC_8H_{17} \\ \qquad\quad | \\ NaO_3S\text{-}CH\text{-}COON(C_4H_{19})_2 \end{array}$$

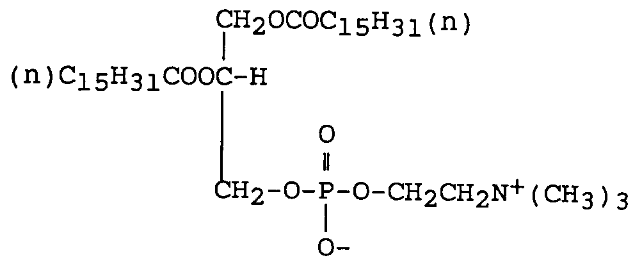
A-17

$$\begin{array}{l} \qquad\quad CH_2COO(CH_2CH_2O)_3CH_2CH(C_2H_5)C_4H_9 \\ \qquad\quad | \\ NaO_3S\text{-}CHCOOH \end{array}$$

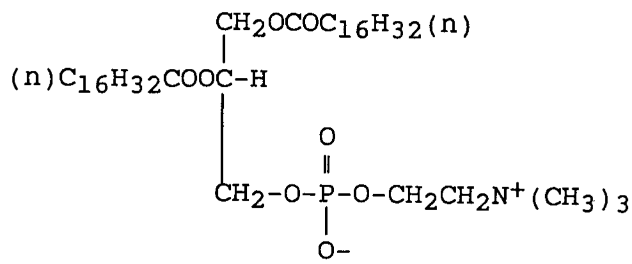
A-18

$$\begin{array}{l} \qquad\quad CH_2\text{-}COOC_{13}H_{27}(i) \\ \qquad\quad | \\ NaO_3S\text{-}CH_2COOC_{13}H_{27}(i) \end{array}$$

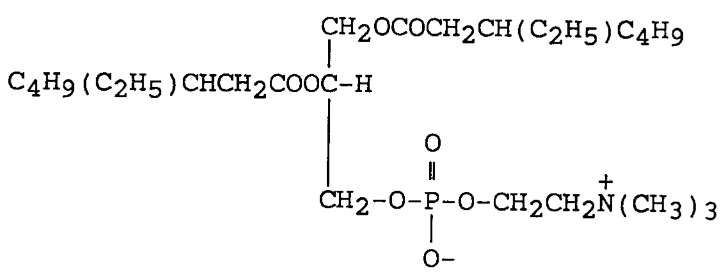
B-1



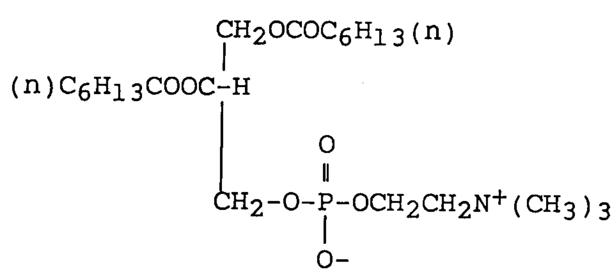
B-2



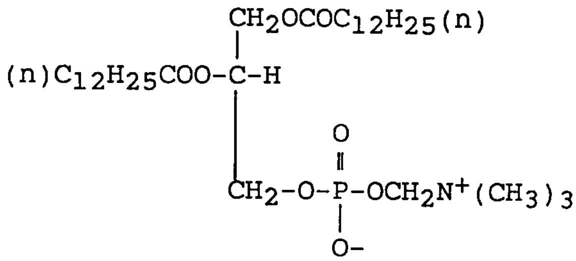
B-3



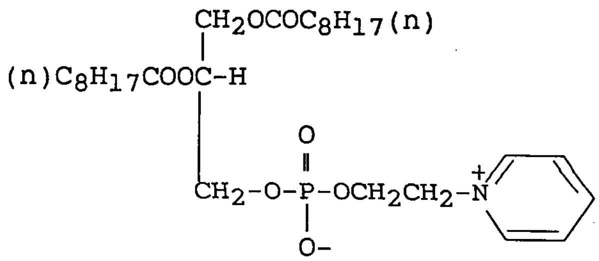
B-4



B-5



B-6



C-1

$CF_3(CF_2)_7SO_2NCH_2CH_2O(CH_2CH_2O)_3(CH_2)_3SO_3Na$
$\quad\quad\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad\quad\quad C_3H_7$

C-2

$CF_3(CH_2)_7SO_2NCH_2CH_2SO_3Na$
$\quad\quad\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad\quad\quad C_3H_7$

C-3

$CH_2COOCH_2(CF_2)_8H$
$|$
$CHCOOCH_2(CF_2)_8H$
$|$
SO_3Na

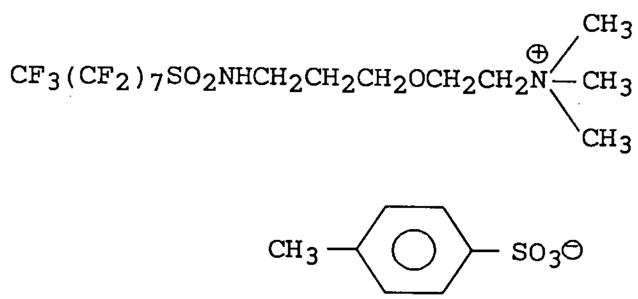
C-4

$$CF_3(CF_2)_7SO_2NHCH_2CH_2\overset{\oplus}{N}(CH_3)_3 \quad I^{\ominus}$$

C-5

$$CF_3(CF_2)_7SO_2N(C_3H_7)CH_2COOk$$

C-6



D-1

$$C_{12}H_{25}O{+}CH_2CH_2O{+}_{10}H$$

D-2

$$C_{16}H_{33}O{+}CH_2CH_2O{+}_{10}H$$

D-3

$$C_{18}H_{37}O{+}CH_2CH_2O{+}_{10}H$$

D-4

$$C_{22}H_{45}O{+}CH_2CH_2O{+}_{10}H$$

D-5

$C_{12}H_{25}O-(CH_2CH_2O)_5H$

D-6

$C_{12}H_{25}O-(CH_2CH_2O)_{15}H$

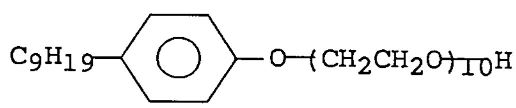
D-7

$C_{12}H_{25}O-(CH_2CH_2O)_{20}H$

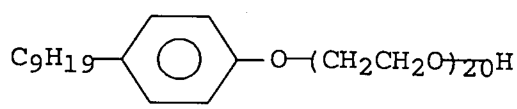
D-8

$C_{12}H_{25}O-(CH_2CH_2O)_{25}H$

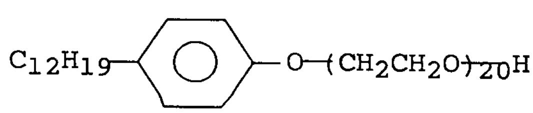
D-9



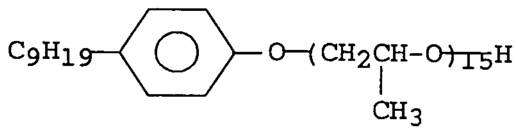
D-10



D-11



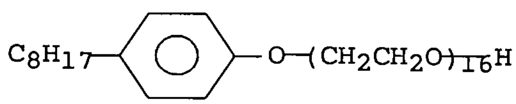
D-12



D-13

$$C_{12}H_{25}-O\!-\!(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H-O)_{10}H$$

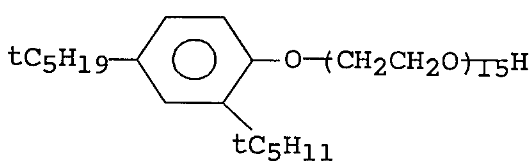
D-14



D-15

$C_{18}H_3COO(CH_2CH_2O)_nH$

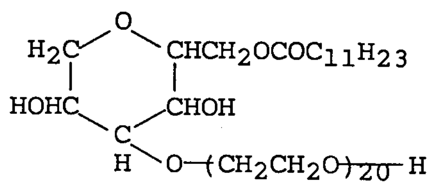
D-16



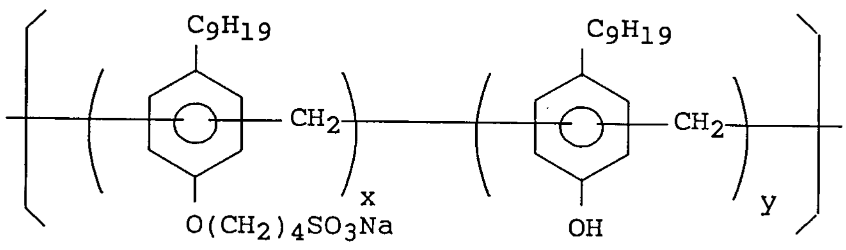
D-17

$$H\!-\!(OCH_2CH_2)_{10}O-\underset{\displaystyle CH_2COOCH_2CH(C_2H_5)C_4H_9}{\underset{|}{C}}HCOOCH_2CH(C_2H_5)C_4H_9$$

D-18



E-1



$x/y = 4/6$
$m = 6.8$

E-2

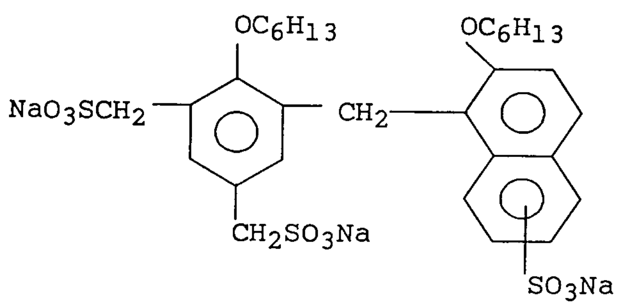
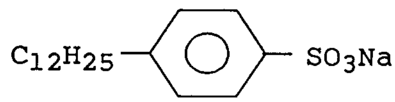
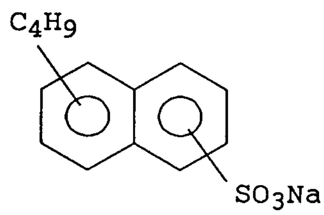


Table C

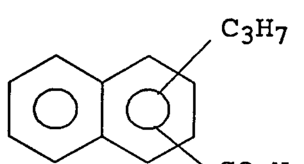


$C_{17}H_{33}CON(CH_3)CH_2CH_2SO_3Na$



$C_{12}H_{25}OSO_3Na$

$$\begin{array}{l} \quad\quad\;\; CH_2COOCH_2CH(C_2H_5)C_4H_9 \\ \quad\quad\;\; | \\ NaO_3S-CHCOOCH_2CH(C_2H_5)C_4H9 \end{array}$$



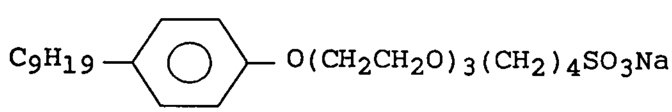
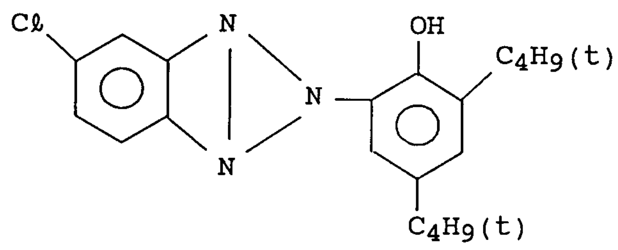
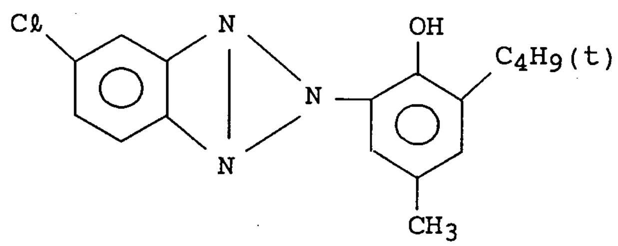


Table D

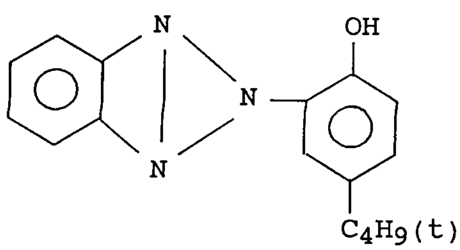
UV-1



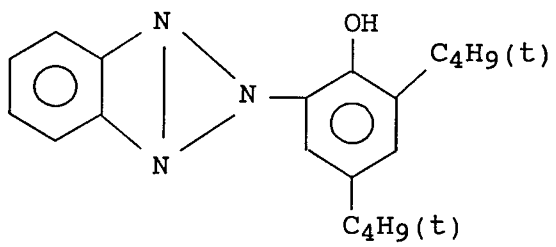
UV-2



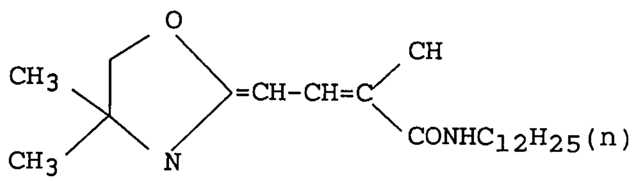
UV-3



UV-4



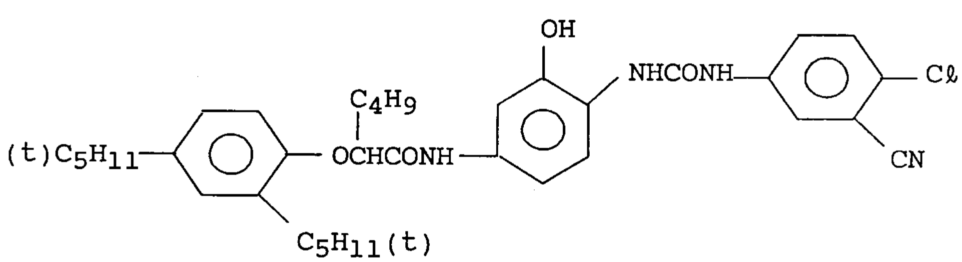
UV-5



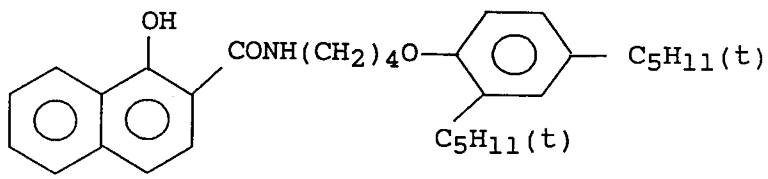
oil-1

oil-2

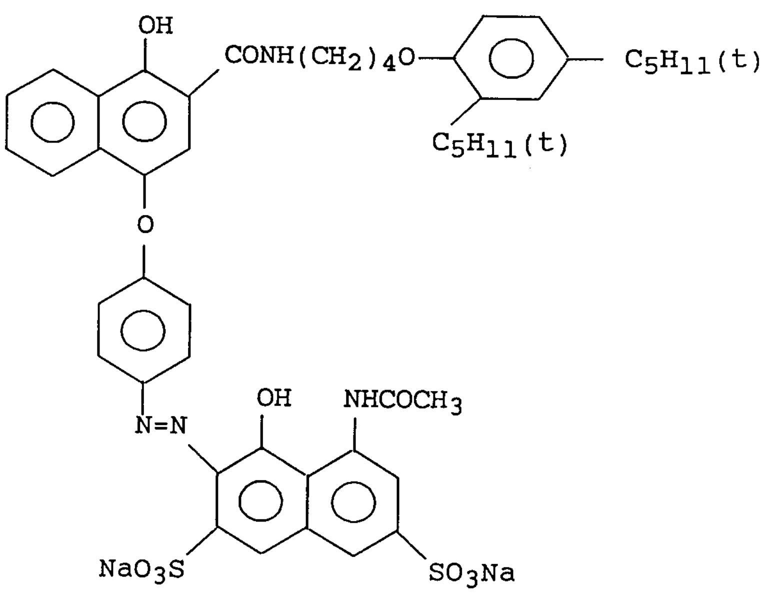
Cp-1



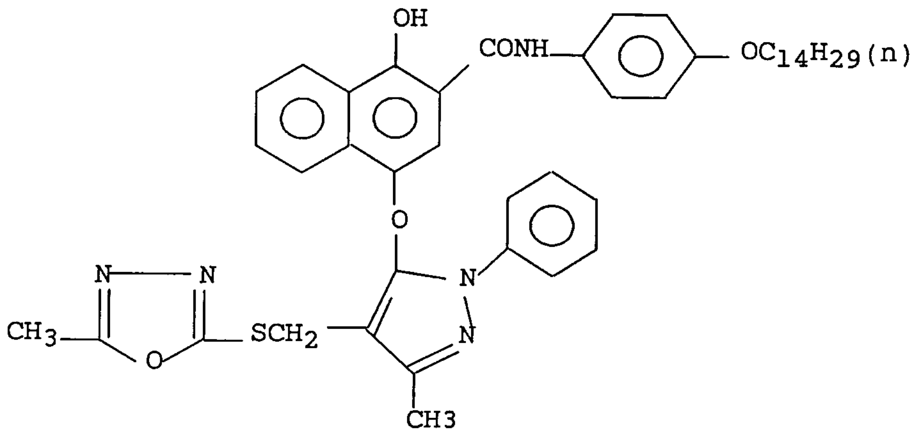
Cp-2


OH
CONH(CH2)4O
C5H11(t)
C5H11(t)

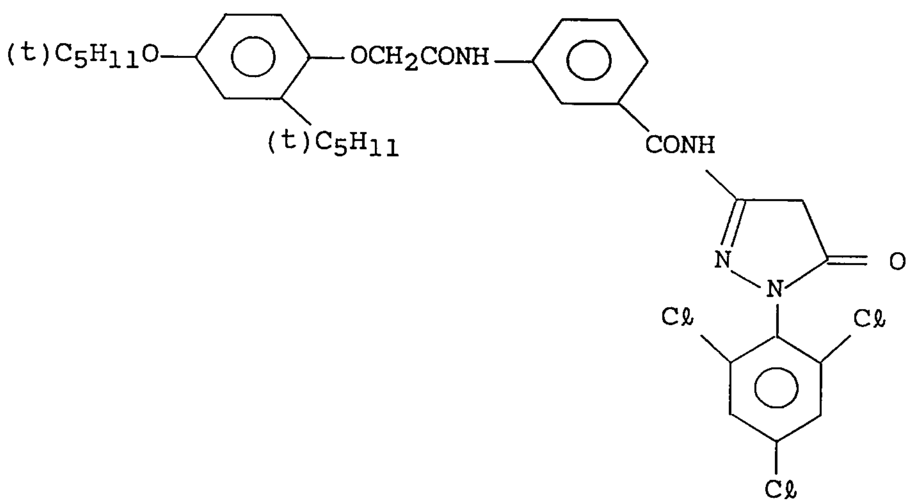
Cp-3


OH
CONH(CH2)4O
C5H11(t)
C5H11(t)
O
N=N
OH
NHCOCH3
NaO3S
SO3Na

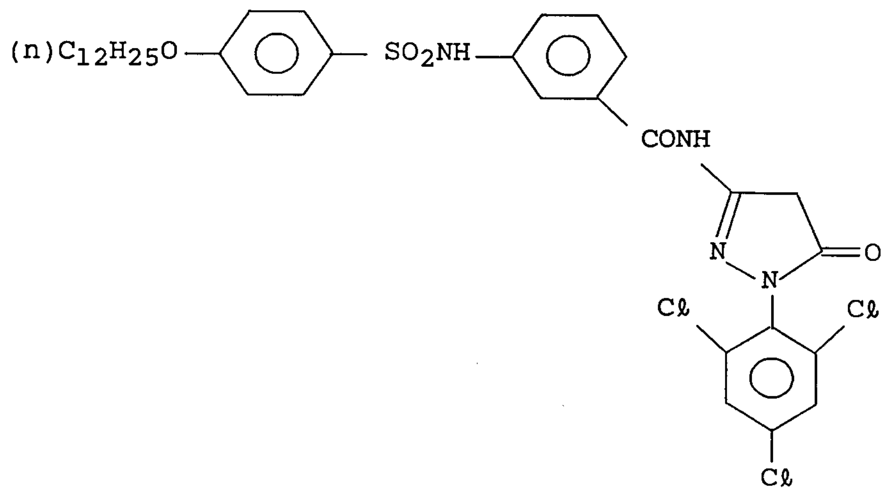
Cp-4


OH
CONH
$OC_{14}H_{29}(n)$
O
N
N
N
N
CH_3
O
SCH_2
CH3

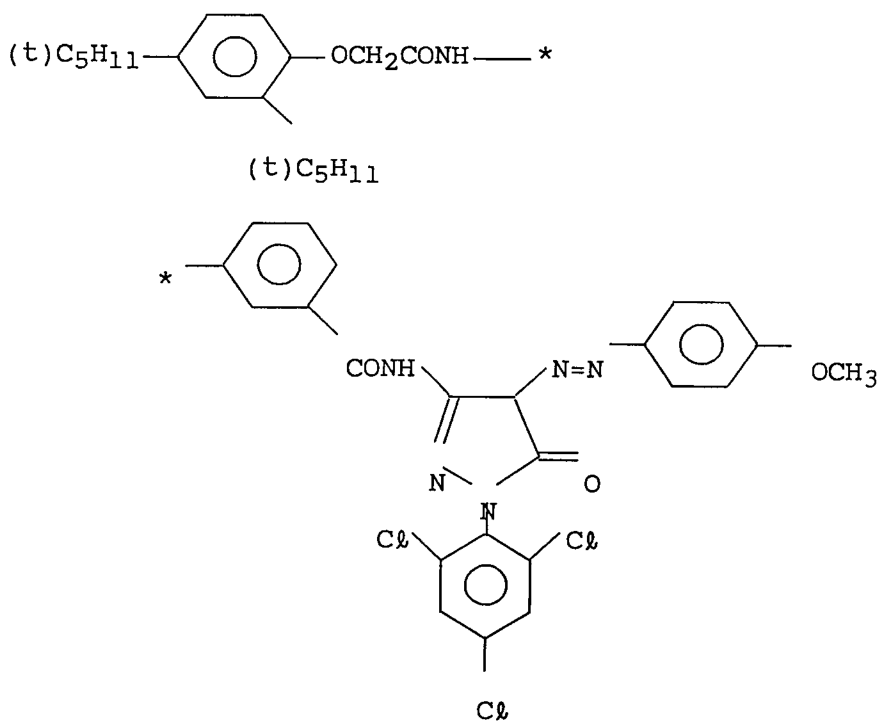
Cp-5


$(t)C_5H_{11}O$
OCH_2CONH
$(t)C_5H_{11}$
CONH
N
N
O
Cℓ
Cℓ
Cℓ

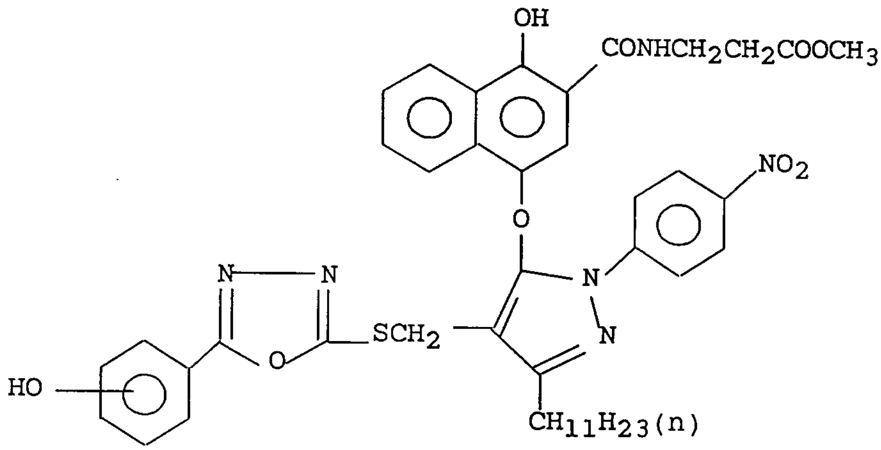
Cp-6


(n)C12H25O
SO2NH
CONH
N
N
O
Cℓ
Cℓ
Cℓ

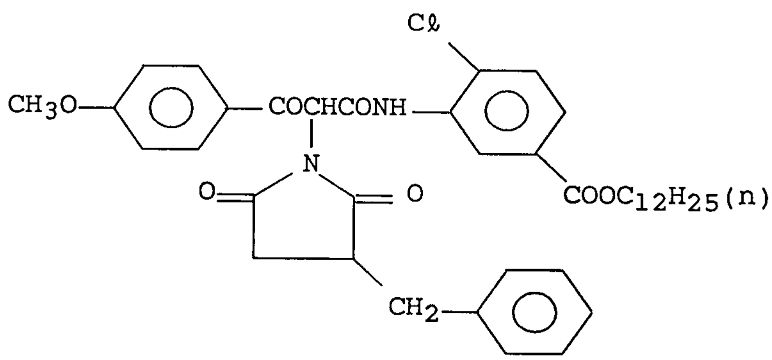
Cp-7


(t)C5H11
OCH2CONH
*
(t)C5H11
*
CONH
N=N
OCH3
N
N
O
Cℓ
Cℓ
Cℓ

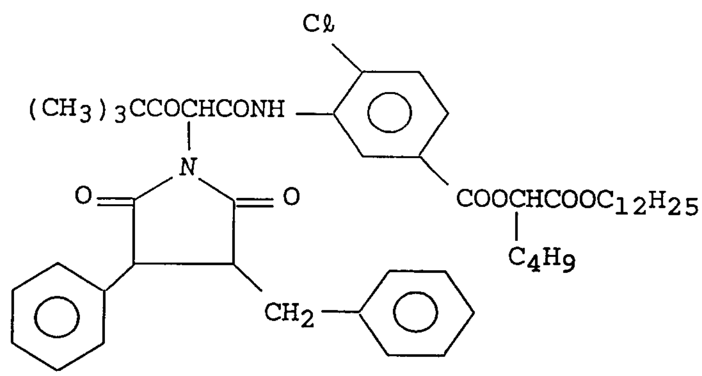
Cp-8



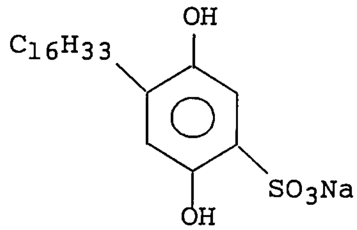
Cp-9



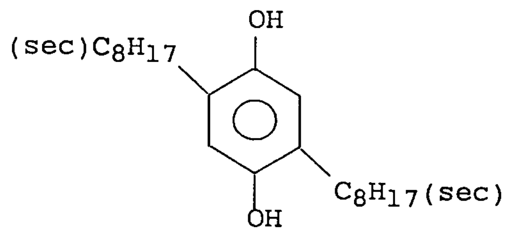
Cp-10



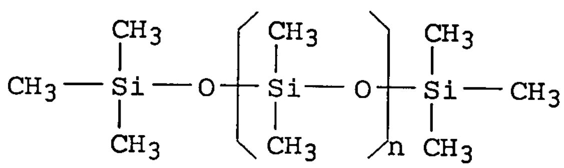
Cpd-11



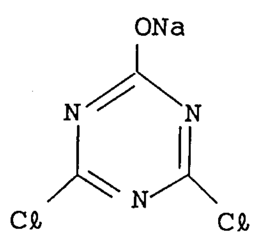
Cpd-12



B-11



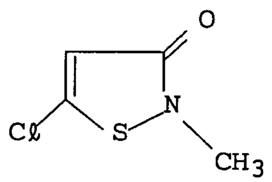
H-11



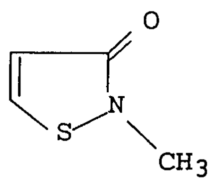
H-12

$$\{((CH_2=CHSO_2CH_2)_2CCH_2SO_2(CH_2)_2\}_2N(CH_2)_2SO_3K$$

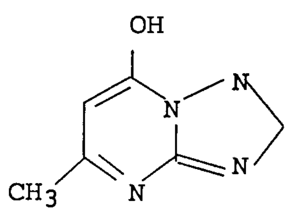
Cpd-15



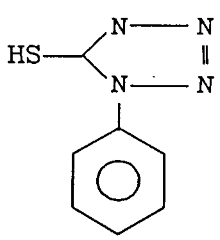
Cpd-16



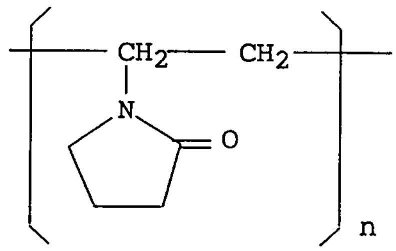
Cpd-17



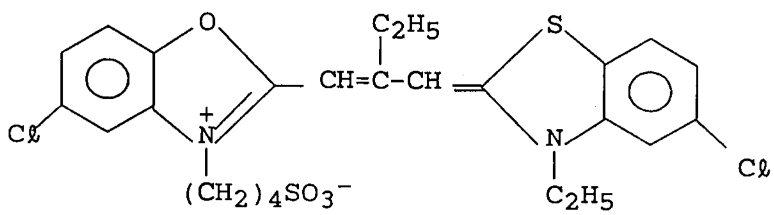
Cpd-18



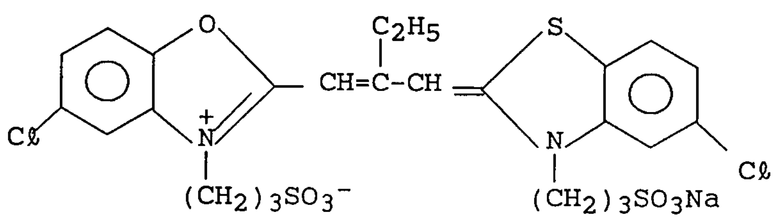
Cpd-19



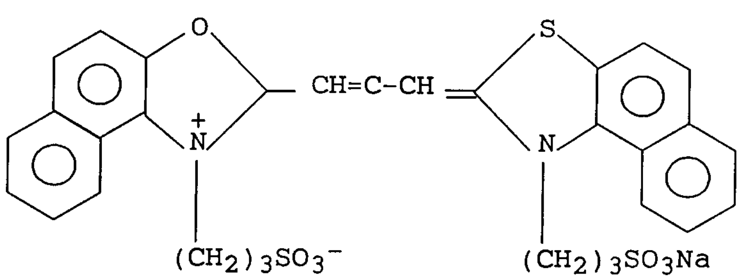
S-1



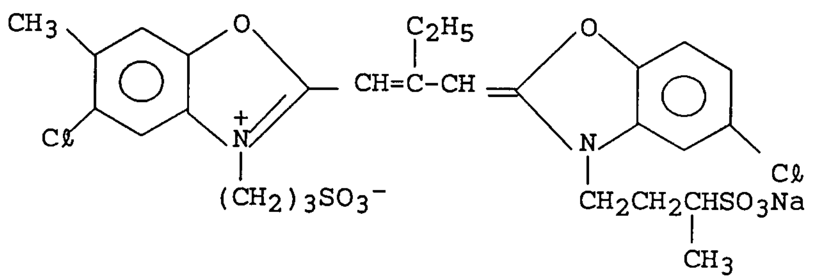
S-2



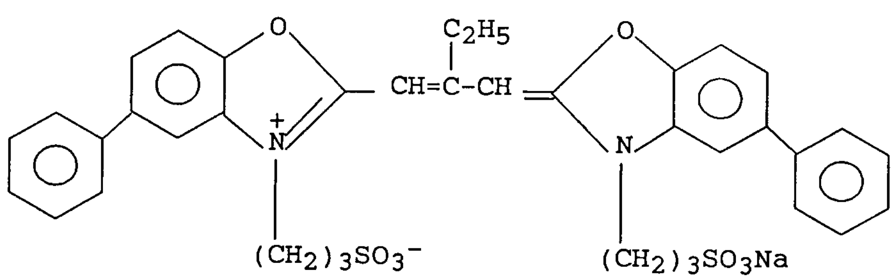
S-3



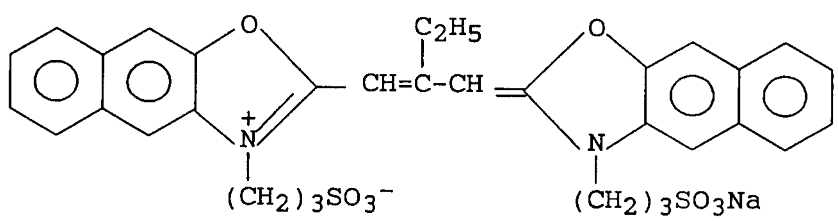
S-4


CH3
O
C2H5
CH=C-CH
O
Cℓ
N
N
Cℓ
(CH2)3SO3−
CH2CH2CHSO3Na
CH3

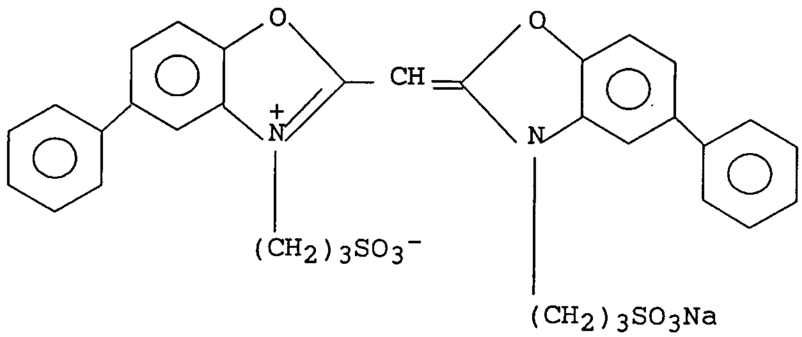
S-5


O
C2H5
CH=C-CH
O
N
N
(CH2)3SO3−
(CH2)3SO3Na

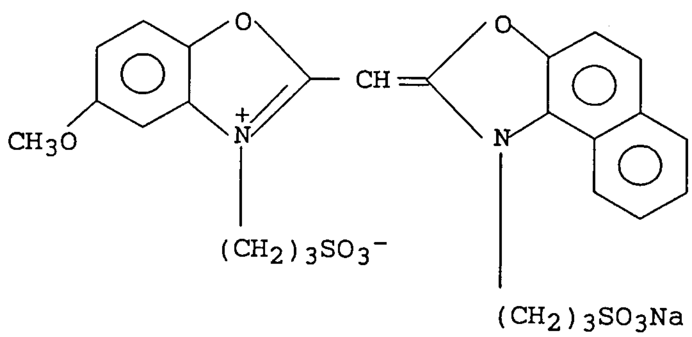
S-6


O
C2H5
CH=C-CH
O
N
N
(CH2)3SO3−
(CH2)3SO3Na

S-7



S-8



Claims

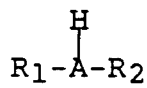
1. A silver halide color photographic light-sensitive material having, on a support, at least one of each of a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, and a red-sensitive silver halide emulsion layer, said light-sensitive material having at least 12 layers simultaneously coated on said support by one coating cycle, said at least 12 layers including said blue-, green-, and red-sensitive silver halide emulsion layers, and said light-sensitive material containing at least one formalin scavenger in a total amount of 0.1 g/m^2 to 0.7 g/m^2 and at least one surfactant in a total amount of 0.1 g/m^2 to 0.7 g/m^2.

2. The material according to claim 1, characterized in that said light-sensitive material contains 0.1 g/m^2 to 0.6 g/m^2 of a surfactant represented by the following formula (A): Formula (A)

   $R\!-\!\!(L)_nSO_3^-M^+$

   where R represents an alkyl group, an aryl group, an aralkyl group, or an alkenyl group, a total number of carbon atoms contained in R being 8 to 36, L represents a divalent coupling group, n represents 0 or an integer from 1 to 10, and M represents hydrogen or a cation.

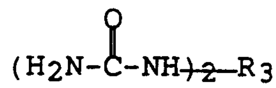
3. The material according to claim 1, characterized in that said formalin scavenger is represented by formula (S):



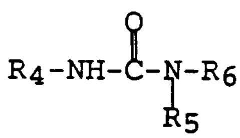
where each of R_1 and R_2 independently represents a hydrogen atom, an alkyl group which may be substituted, an aryl group which may be substituted, an acyl group, an alkoxycarbamoyl group, a carbamoyl group, an imino group, or an amino group; R_1 and R_2 may form a ring or a fused ring, with the proviso that when R_1 and R_2 do not form a ring, at least one of R_1 and R_2 is an acyl group, a carbamoyl group, or an amino group; and A represents > CH- or > N-.

4. The material according to claim 1, characterized in that said formalin scavenger is represented by the following formula (S-I), (S-II), (S-III), or (S-IV):

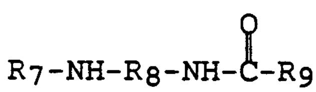
Formula (S-I)



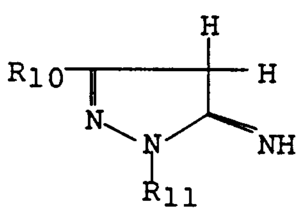
Formula (S-II)



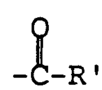
Formula (S-III)



Formula (S-IV)



where, R_3 represents a divalent alkyl group; each of R_4, R_5, and R_7 independently represents a hydrogen atom, an alkyl group,

or 

(where R' represents a hydrogen atom); R_6 represents an alkyl group or an amino group; and R_9 represents an alkyl group which may have a substituent group; R_4 and R_6 may form a ring or a fused ring, and R_7 and R_9 may form a ring; R_8 represents a carbonyl group or a carboimidoyl group; and R_{10} represents a hydrogen atom, an alkyl group, a cyclohexyl group, a phenyl group, an aralkyl group, an alkoxyl group, an aryloxy group, a carbamoyl group, an alkoxycarbonyl group, or a cyano group, all of which may be substituted, if appropriate; and R_{11} represents a hydrogen atom, an alkyl group, a cyclohexyl group, a phenyl group, an aralkyl group, a heterocyclic group, a benzoyl group, a sulfonalkyl group, a sulfonaryl group, a carboxyalkyl group, a carbazoyl group, or a thiocarbamoyl group.

5. The material according to claim 1, characterized in that the amount of said formalin scavenger is 0.1 g/m^2 to 0.5 g/m^2.

6. The material according to claim 1, characterized in that the amount of said formalin scavenger is 0.1 g/m^2 to 0.3 g/m^2.

7. The material according to claim 1, characterized in that all layers on said support are simultaneously coated by one coating cycle.

8. The material according to claim 1, characterized in that 14 or more layers are simultaneously coated by one coating cycle.

9. The material according to claim 1, characterized in that the layers are coated such that a viscosity of a coating solution for a layer adjacent the layer closest to said support is adjusted to be 1.5 or more times a viscosity of a coating solution for the layer closest to said support.

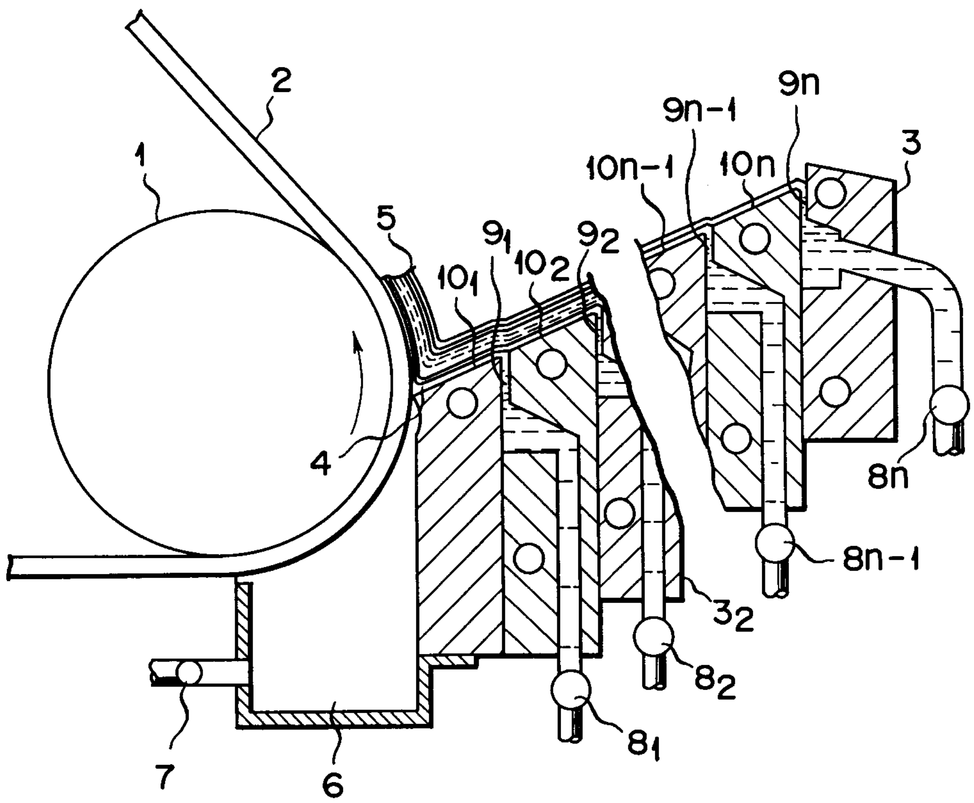
10. The material according to claim 1, characterized in that the layers are coated such that a viscosity of a coating solution for a layer adjacent the layer closest to said support is adjusted to be 1.8 to 5 times a viscosity of a coating solution for the layer closest to said support.

11. The material according to claim 1, characterized in that the layers are coated by a slide hopper coating apparatus, while applying a bead back pressure.

12. The material according to claim 1, characterized in that at least one of said blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers is comprised of at least three layers of the same color sensitivity, but of different speed.

13. The material according to claim 1, characterized in that said material contains silver halides in a total amount of 2.5 g/m^2 to 8 g/m^2 in terms of silver.

14. The material according to claim 1, characterized in that said material contains silver halides in a total amount of 2.5 g/m^2 to 6 g/m^2 in terms of silver.



F I G. 1

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 6427

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-4 001 024 (DITTMAN ET AL.) * column 2, line 64 - column 3, line 3 * * * column 7, line 8 - line 19 * * * column 7, line 58 - line 68 * * * column 8, line 33 - line 66; figure 1 * * – – –	1-14	G 03 C 1/74 G 03 C 1/38 G 03 C 7/392
Y	US-A-4 894 318 (ARAKAWA ET AL.) * column 9, line 24 - line 32 * * * column 10, line 61 - line 63 * * * column 11, line 34 - line 42 * * * column 12, line 48 - line 52 * * – – –	1,3-6	
Y	FR-A-2 215 269 (KODAK) * page 4, line 7 - line 14 * * * page 7, line 36 - page 8, line 7; figure 1 * * – – –	1,7-11	
Y	EP-A-0 285 176 (FUJI) * page 75, line 16 - page 78, line 5 * * – – –	1,12-14	
Y	PATENT ABSTRACTS OF JAPAN vol. 12, no. 76 (P-675)(2923) 10 March 1988 & JP-A-62 215 271 (FUJI) 21 September 1987 * abstract * * – – –	1,2	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
P,X	EP-A-0 443 528 (FUJI) * page 19, line 32 - page 20, line 58 * * * page 22, line 13 - line 15 * * * page 25, line 30 - page 32, line 38 * * * page 43, line 22 - line 30 * * * page 45, line 30 - line 48; figure * * – – – – –	1-14	G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	03 January 92	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same catagory
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention

E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document