(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 514 868 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **92108520.5**

(51) Int. Cl.^{5}: **G03C 5/395**, G03C 7/44

(22) Date of filing: **20.05.92**

(30) Priority: **24.05.91 JP 149791/91**

(43) Date of publication of application:
25.11.92 Bulletin 92/48

(84) Designated Contracting States:
DE FR GB NL

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(54) Method for processing a silver halide photographic light-sensitive material and method for recycling a processing solution.

(57) A process of recycling a processing solution of a silver halide photographic light-sensitive material is disclosed. The process comprises the steps of processing the material with the processing solution, precipitating a silver compound in the processing solution using a precipitant, removing the precipitated silver compound to regenerate the solution, and recycling the solution.

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FIELD OF THE INVENTION

The present invention relates to a method for processing a silver halide light-sensitive material and a method for recycling a processing solution. More particularly, the present invention relates to a method for processing a silver halide light-sensitive material and a method for recycling a processing solution, which not only enable the recovery of silver from a processing solution but also prevent yellow stains even when the recycling is repeated many times.

BACKGROUND OF THE INVENTION

It is well known that silver is recovered from a photographic processing solution having a fixing capability, and that such a fixing-capable processing solution is recycled.

For example, Japanese Patent O.P.I. Publication No. 14849/1980 discloses a technique to utilize the so-called electrolytic method which comprises electrodialysis to recover silver and recycling processing solutions. Japanese Patent O.P.I. Publication No. 69626/1981 discloses a method, in which an electrolyzer is partitioned into a cathode chamber and an anode chamber by a membrane of ion exchange resin, in order that the recovery of silver and the recycling of fixing solutions are carried out in the cathode chamber and the recycling of bleaching solutions is performed in the anode chamber.

In both cases, however, the ion exchange resin membrane used as a diaphragm cannot last long and has to be replaced at least once a year, which needs an intricate replacing work and a high replacing cost owing to the expensiveness of ion exchange resin membranes. Further, the above electrolytic method requires additional processes such as analysis of composition of a processing solution and replenishment of shortages, because a processing solution after silver recovery differs in composition from that before silver recovery.

There is another problem in setting the condition of silver recovery condition. That is, once an excessive electrolytic current is applied to a processing solution, precipitates of silver sulfide are formed and, therefore, the processing solution becomes unusable for fear of staining a light-sensitive material with such precipitates.

Further, it is also found that photographic properties of a light-sensitive material are fatally injured by stains and fading of cyan dyes as the number of recycling cycles increases.

On the other hand, Japanese Patent Examined Publication No. 24822/1977 discloses a method for precipitating metal silver by reducing silver ions with dithionic acid at a pH of 8.5 to 10. This technique, however, cannot be practiced within doors because of an unpleasant odor generated. Moreover, the use of a fixing solution recycled by this method is liable to cause yellow stains.

SUMMARY OF THE INVENTION

Accordingly, the object of the present invention is to provide a method for processing a silver halide photographic light-sensitive material and a method for recycling a processing solution, which can recycling simply and effectively a waste solution of a processing solution for silver halide photographic light-sensitive materials, and has no adverse effect on the photographic properties of a light-sensitive material when a recycled solution is reused as a processing solution or as a replenisher thereof.

The present inventors have made a close study to achieve the above object and found that a precipitating treatment, or a recycling treatment with a precipitant, can decrease the formation of stains and the fading of cyan dyes even when a light-sensitive material is processed even with a repeatedly recycled, fixing-capable processing solution.

That is, the method for recycling a processing solution according to the invention is characterized in that a waste liquid of a silver halide light-sensitive material processing solution is reclaimed by removing silver compounds through a precipitating treatment, and that the reclaimed solution is then reused as a portion or all of the above processing solution or replenisher.

Further, in continuous processing of a silver halide photographic light-sensitive material using a processing solution having a fixing capability and a replenisher thereof, the method for processing a silver halide light-sensitive material according to the invention is characterized in that a waste liquid of a processing solution having a fixing capability is subjected to a precipitating treatment to remove silver compounds, and that the processing solution after the precipitating treatment is then reused as a portion or all of the above replenisher.

In practicing the method according to the invention, it is preferable that a compound of which the solubility product with silver ion is not more than 10^{-9} be used in the precipitating treatment, that a reducing agent be used in the precipitating treatment, that said reducing agent be selected from boron hydride salts, aluminium hydride salts and hydrosulfite salts, and that the surface tension of the above processing solution having a fixing capability be not more than 60 dyn/cm.

DETAILED DESCRIPTION OF THE INVENTION

In the invention, a silver halide light-sensitive material processing solution recovered for reuse may be any of a color developing solution, a bleaching solution, a fixing-capable processing solution, a stabilizing solution, a rinsing solution and a prewashing solution. But processing solutions (bleach-fixing solution and fixing solution) containing silver compounds in large amounts are preferred.

The reclaimed solution after silver removal may be used as a processing solution again, or as a replenisher in continuous processing.

When the reclaimed solution is used as a replenisher, the solution may be used without any further adjustment, or shortages of chemicals estimated in advance may be added thereto as reactivators, or shortages of chemicals may be first confirmed by analyzing the component of the solution according to a usual method and then replenished thereto. In each case, the pH is adjusted as occasion demands.

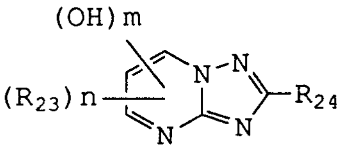
The precipitating treatment according to the invention, or the recycling treatment using a precipitant, is carried out in the presence of a compound of which the solubility product with silver ion is not more than 10^{-9}, preferably not more than 10^{-10}, and more preferably not more than 10^{-11}.

As a compound of which the solubility product with silver ion is not more than 10^{-9}, there can be used tetrazaindene derivatives, 6-aminopurine derivatives and sulfur compounds. Of them, sulfur compounds are particularly preferred.

The solubility product used in the invention has the same meaning as the general meaning described in Kagaku Daijiten (Chemical Encyclopedia), 14th reduced-size edition, vol. 9, p. 399, Kyoritsu Shuppan, September 15, 1972, and shows a product of the concentration (gram ion/liter) of the compound and that of silver ion at 25 ° C when a sparingly water-soluble silver salt is formed between silver ions and the compound.

Usable tetrazaindene derivatives include those which are used as a stabilizer for silver halide photographic emulsion, and those represented by the following Formula I are particularly effective.

Formula I

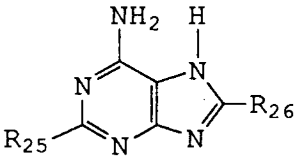


The description of the formula is the same as that given from the 12th line to the 15th line on the 11th page of Japanese Patent O.P.I. Publication No. 252656/1991.

Among the useful tetrazaindene derivatives represented by Formula I, particularly useful ones are those denoted by A-1 to A-8 from the 1st line on the 12th page to the 7th line on the 13th page of Japanese Patent O.P.I. Publication No. 252656/1991. These compounds can be synthesized by a conventional method. Among these compounds, ones having a hydroxyl group at the 4-position are preferred, and ones having a hydroxyl group at the 4-position and an alkyl or aryl group at the 6-position are particularly preferred.

The above 6-aminopyrine derivative includes ones known as a stabilizer for photographic silver halide emulsions, and ones represented by the following Formula II are preferred.

Formula II



The description of the formula is the same as that given from the 13th line on the 13th page to the 2nd line on the 14th page of Japanese Patent O.P.I. Publication No. 252656/1991.

Among the effective 6-aminopyrine derivatives represented by Formula II, particularly effective ones are those denoted by B-1 to B-7 from the 3rd line to the 20th line on the 14th page of Japanese Patent O.P.I. Publication No. 252656/1991.

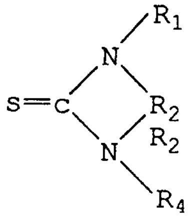
These tetrazaindene derivatives and 6-aminopyrine derivatives are used in an amount of preferably 0.5 to 500 g, especially 1.0 to 400 g per liter of processing solution.

The sulfur compounds effectively used in the invention include sulfides, polysulfides, thiourea compounds and other sulfur compounds.

Examples of the sulfide include alkali metal sulfides such as potassium sulfide, sodium sulfide and ammonium sulfide. Examples of the polysulfide include those compounds which are described in Kogyo Kagaku Zasshi, vol. 63, No. 3, pp. 482-485 (1960). The addition amount of these sulfides or polysulfides is not particularly limited. But these compounds are used at a concentration not less than 1.0 time, preferably not less than 1.5 times, and especially not less than 2.0 times the concentration of silver ion contained in a waste processing solution.

Usable thiourea compounds are those represented by the following Formula III.

Formula III



The description of the formula, the detailed description of R1, R2, R3 and R4, and the examples of the compound are the same as those described from the 1st line on the 16th page to the 3rd line on the 20th page of Japanese Patent O.P.I. Publication No. 252656/1991. The addition amount thereof is the same as that of the above sulfides or polysulfides.

Other usable sulfur compounds include those described in Nikkakyo Geppo, vol. 28, p. 7, May 1975 issue; Chem. Eng., p. 49, Sept. 29, 1975 issue; Japanese Patent Examined Publication Nos. 38039/1974, 18474/1975; Japanese Patent O.P.I. Publication Nos. 7776/1975, 34084/1973, 22374/1973, 17485/1973, 111765/1976, 282841/1986; and GB 1411985. Typical examples thereof are, for example, dithiocarbamic acid compounds, polythiols, methyl mercaptan, ethyl mercaptan, propyl mercaptan, isopropyl mercaptan, allyl mercaptan, benzyl mercaptan, thioglycol, thiolactic acid and α-thiolpropionic acid.

Some of these compounds are commercially available under the tradenames, for example, ALM-648 (a water-soluble heavy metal ion fixative made by Nippon Soda Co.) and Oritol S (made by Oriental Giken Kogyo Co.).

In the precipitating treatment of the invention, it is preferable that a flocculant be used together with the above compound of which solubility product with silver ion is not more than 10^{-9}, and it is particularly preferable that such a flocculant be a high-molecular flocculant.

High-molecular flocculants fall into the anionic type, the cationic type and the nonionic type. Ones usable in the invention are described from the 1st line on the 21th page to the 8th line on the 22nd page of Japanese Patent O.P.I. Publication No. 252656/1991. When these flocculants are used, there may be jointly employed a flocculation aid such as kaolin, bentonite, acid clay, fly ash, sodium silicate, soda ash, slaked lime or wood powder.

When the method according to the invention is carried out, a precipitate appears after the addition of the compound of which solubility product with silver ion is not more than 10^{-9}, or after the addition of a flocculent under the necessity. Then, the precipitate is separated from a processing solution to recover the solution for recycling. There are the following three modes for recycling.

(1) The solution is allowed to stand, then the supernatant is used without any further adjustment.
(2) The solution is allowed to stand, then the supernatant is filtered or centrifuged for reuse.
(3) The solution containing the precipitate is filtered or centrifuged as it is and reused.

As a filtering means, there can be employed any of filtration using a filter medium (sand, filter paper, filter cloth, sintered glass or sintered metal), ultrafiltration (including use of flat membranes or hollow fiber membranes), reverse osmosis, and an activated carbon treatment. A method which combines centrifugation and filtration can also be used. Further, dehydration of sludge may be performed by use of a conventional dehydration means, such as a precoat filter, instead of centrifugation.

As reducing agents suitable for the invention, there may be employed any reducing agent as long as it has a potential more negative than -0.50 V as a standard oxidation reduction potential. The preferred reducing agent is one having a potential more negative than -10 V.

Preferable examples thereof include boron hydride salts (salts of BH_4^-), aluminium hydride salts (salts of AlH_4^-), hydrosulfite salts (salts of $S_2O_8^{2-}$) and Rongalite.

These compounds are used in amount of preferably 0.5 to 500 g and especially 1.0 to 400 g per liter of a processing solution.

In the invention, the surface tension of the above fixing-capable processing solution is preferably not more than 60 dyn/cm, especially 8 to 55 dyn/cm. With a surface tension set as above, stains can be effectively prevented.

The surface tension can be measured by a general method described, for example, in K. Kitahara, S. Hayano and I. Hara, Method for Analyzing and Testing Surface Active Agents, Kodansha Co., March 1, 1982. In the invention, values of the surface tension measured at 20° C by such a general method are used.

One method for making the surface tension of a processing solution less than 60 dyn/cm at 20° C is to use a water-soluble surfactant. Usable surfactants include those which are described, for example, in Japanese Patent O.P.I. Publication Nos. 40824/1981, 116031/1981, 130744/1981, 199346/1983, 17551/1984, 126533/1984, 50148/1986, 154153/1989, 316743/1989 and Japanese Patent Application No. 341357/1989.

In the invention, it is preferable that the fixing-capable processing solution contain the optical whitening agent described paragraph Nos. 0038 to 0042 of Japanese Patent Application No. 59466/1991.

In the invention, the fixing-capable processing solution is not particularly limited except the above composition and may contain additives similar to those used in the bleach-fixing solution or the fixing solution described in Japanese Patent Application No. 51226/1990.

Further, the bleaching solution, the color developing solution and the stabilizing solution may be analogous to those described in Japanese Patent Application No. 51226/1990, or may be similar to the bleaching solution, the color developing solution and the stabilizing solution described in Japanese Patent O.P.I. Publication No. 48548/1988.

The invention can be applied to a light-sensitive material to be processed by the so-called coupler-in-emulsion process as well as a light-sensitive material to be processed by the so-called coupler-in-developer process, and can be applied to any of color paper, color negative film, color positive film, color reversal film for slides, color reversal film for movies, color reversal film for TVs and color reversal paper.

EXAMPLES

The invention is hereunder described in detail with the examples.

Example 1

A multilayered color light-sensitive material was prepared by forming the layers shown below on the titanium-oxide-containing side of a paper support coated with polyethylene on one side and with titanium-oxide-containing polyethylene on the other side. The coating solutions were prepared as follows:

1st coating solution

A mixture of 26.7 g of yellow coupler (Y-1), 10.0 g of dye image stabilizer (ST-1), 6.67 g of dye image stabilizer (ST-2), 0.67 g of additive (HQ-1) and 6.67 g of high boiling solvent (DNP) was dissolved in 60 ml of ethyl acetate. The solution was dispersed with a supersonic homogenizer in 220 ml of 10% gelatin solution containing 7 ml of 20% surfactant (SU-1) solution to prepare a yellow coupler dispersion. The dispersion was then mixed with a blue-sensitive silver halide emulsion (containing 10 g of silver) prepared under the following conditions, so that the 1st coating solution was obtained.

The 2nd to the 7th coating solutions were prepared in a similar manner as in the above.

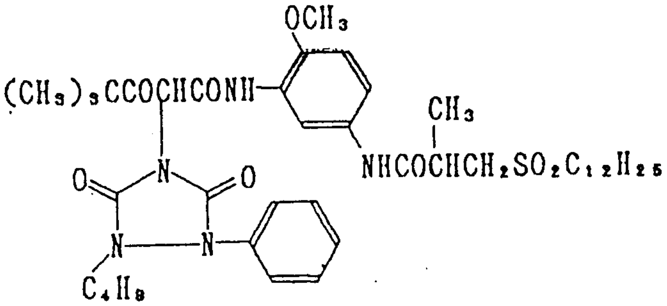
In addition, hardener (H-1) was added to the 2nd and 4th layer and hardener (H-2) to the 7th layer. Surfactants (SU-1) and (SU-2) were employed as coating aids to adjust the surface tension. The layer configuration of the color light-sensitive material was as follows:

Layer	Composition	Addition amount (g/m^2)
7th layer (protective layer)	gelatin	1.0
6th layer (UV absorbing layer)	gelatin	0.4
	UV absorbent (UV-1)	0.10
	UV absorbent (UV-2)	0.04
	UV absorbent (UV-3)	0.15

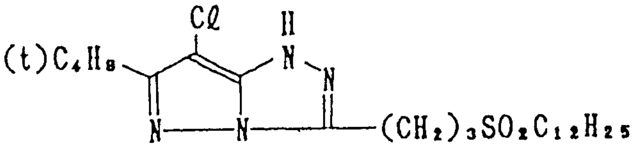
	antistain agent (HQ-1)	0.01
	DNP	0.2
	PVP	0.03
	anti-irradiation dye (AI-2)	0.02
5th layer (red-sensitive layer)	gelatin	1.30
	red-sensitive silver chlorobromide emulsion (Em C), in terms of silver	0.21
	cyan coupler (C-1)	0.17
	cyan coupler (C-2)	0.25
	dye image stabilizer (ST-1)	0.20
	antistain agent (HQ-1)	0.01
	HBS-1	0.20
	DOP	0.20
4th layer (UV absorbing layer)	gelatin	0.94
	UV absorbent (UV-1)	0.28
	UV absorbent (UV-2)	0.09
	UV absorbent (UV-3)	0.38
	antistain agent (HQ-1)	0.03
	DNP	
3rd layer (green-sensitive layer)	gelatin	1.40
	green-sensitive silver chlorobromide emulsion (Em B), in terms of silver	0.17
	magenta coupler (M-1)	0.33

	dye image stabilizer (ST-3)	0.15
	dye image stabilizer (ST-4)	0.15
	dye image stabilizer (ST-5)	0.15
	DNP	0.20
	anti-irradiation dye (AI-1)	
2nd layer (intermediate layer)	gelatin	1.20
	antistain agent (HQ-2)	0.12
	DIDP	0.15
1st layer (blue-sensitive layer)	gelatin	1.20
	blue-sensitive silver chlorobromide emulsion (Em A), in terms of silver	0.26
	yellow coupler (Y-1)	0.77
	dye image stabilizer (ST-1)	0.30
	dye image stabilizer (ST-2)	0.20
	antistain agent (HQ-1)	0.02
	anti-irradiation dye (AI-3)	0.01
	DNP	0.20
Support	polyethylene-laminated paper	

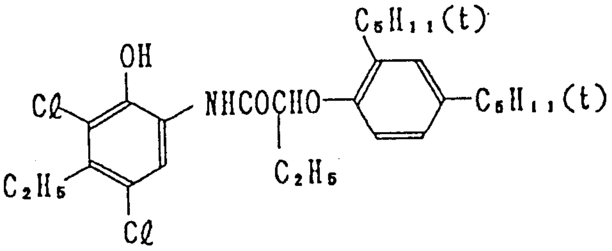
Y - 1



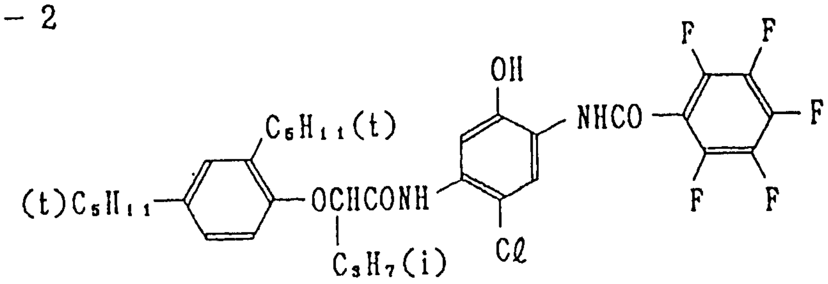
M - 1



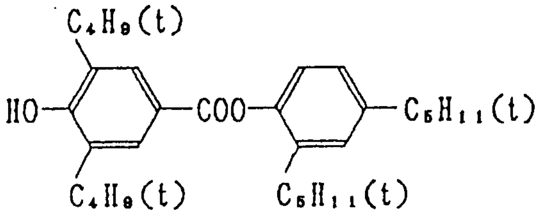
C - 1



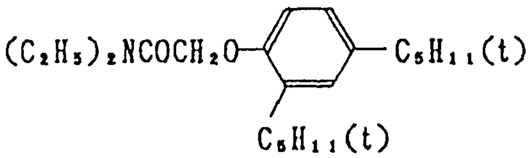
C - 2



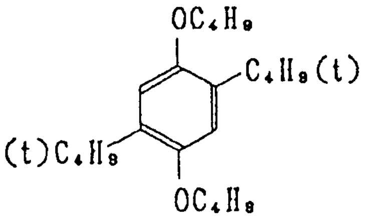
ST-1



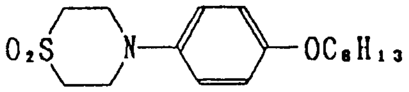
ST-2



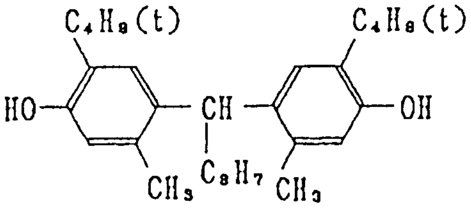
ST-3



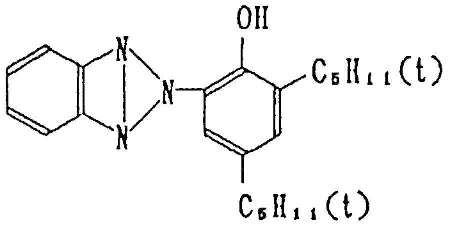
ST-4



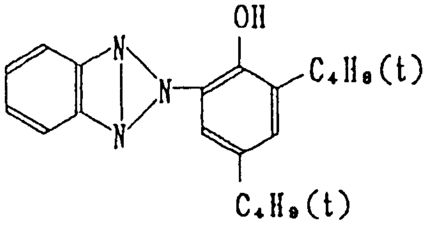
ST-5



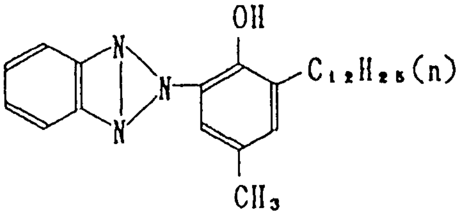
UV-1



UV-2



UV-3



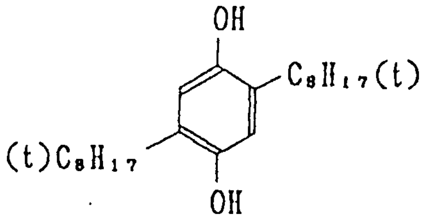
DOP: dioctyl phthalate

DNP: dinonyl phthalate

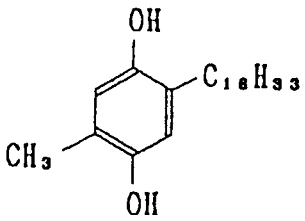
DIDP: diisodecyl phthalate

PVP: polyvinyl pyrrolidone

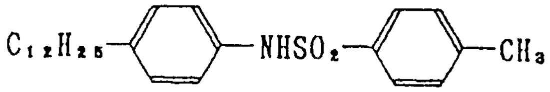
HQ-1



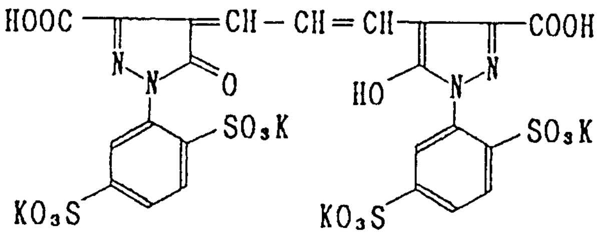
HQ-2



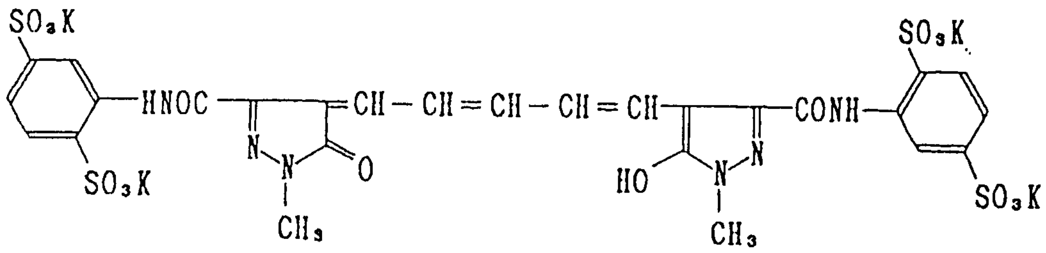
HBS-1



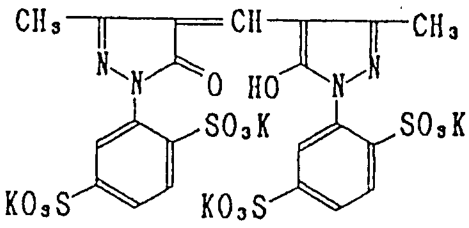
AI-1



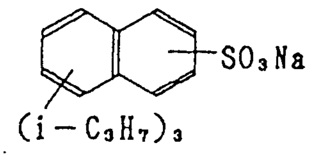
AI-2



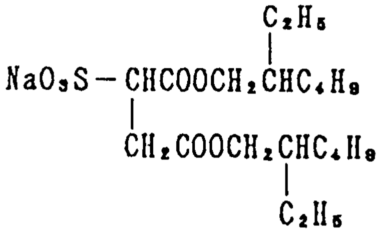
AI-3



SU-1

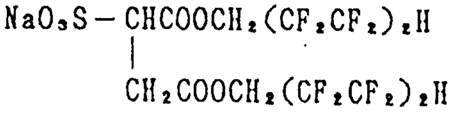


SU-2



$$\mathrm{NaO_3S-\underset{\displaystyle CH_2COOCH_2\underset{\displaystyle C_2H_5}{\underset{|}{C}}HC_4H_9}{\underset{|}{C}}HCOOCH_2\overset{\displaystyle C_2H_5}{\overset{|}{C}}HC_4H_9}$$

SU-3

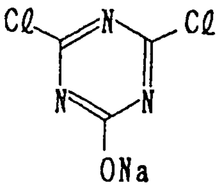


$$\mathrm{NaO_3S-\underset{\displaystyle CH_2COOCH_2(CF_2CF_2)_2H}{\underset{|}{C}}HCOOCH_2(CF_2CF_2)_2H}$$

H-1

$C(CH_2SO_2CH=CH_2)_4$

H-2



Preparation of blue-sensitive silver halide emulsion

To 1000 ml of 2% aqueous gelatin solution kept at 40° C were simultaneously added the following solutions A and B over a period of 30 minutes, while controlling the pAg at 6.5 and the pH at 3.0. Then, the following solutions C and D were simultaneously added thereto over a period of 180 minutes, while controlling the pAg at 7.3 and the pH at 5.5.

The control of the pAg was carried out by the method disclosed in Japanese Patent O.P.I. Publication No. 45437/1984, and that of the pH was made by use of sulfuric acid or an aqueous solution of sodium hydroxide.

Solution A	
Sodium chloride	3.42 g
Sodium bromide	0.03 g
Water was added to make	200 ml

Solution B	
Silver nitrate	10 g
Water was added to make	200 ml

Solution C	
Sodium chloride	102.7 g
Sodium bromide	1.0 g
Water was added to make	600 ml

Solution D	
Silver nitrate	300 g
Water was added to make	600 ml

After the addition, the resulting silver halide emulsion was desalted using a 5% aqueous solution of Demol N made by Kao Atlas Co. and a 20% aqueous solution of magnesium sulfate and then mixed with an aqueous gelatin solution. The emulsion, EMP-1, prepared as above was comprised of monodispersed cubical grains having an average grain size of 0.85μm, a grain size distribution variation coefficient (σ/r) of 0.07 and a silver chloride content of 99.5 mol%.

Subsequently, EMP-1 was chemically sensitized at 50 °C for 90 minutes using the following chemicals to obtain a blue-sensitive silver halide emulsion, Em-B.

Sodium thiosulfate	0.8 mg/mol Ag X
Chloroauric acid	0.5 mg/mol Ag X
Stabilizer (STAB-1)	6 × 10-4 mol/mol Ag X
Sensitizing dye (BS-1)	4 × 10-4 mol/mol Ag X
Sensitizing dye (BS-2)	1 × 10-4 mol/mol Ag X

Preparation of green-sensitive silver halide emulsion

An monodispersed cubical silver halide emulsion, EM-2, was prepared in the same procedure as in EMP-1, except that the addition time of solutions A and B and that of solutions C and D were changed. EM-2 was comprised of grains having an average grain size of 0.43 μm, a grain size distribution variation coefficient (σ/r) of 0.08 and a silver chloride content of 99.5 mol%.

EMP-2 was chemically sensitized at 55 °C for 120 minutes using the following chemicals to obtain a green-sensitive silver halide emulsion, Em-G.

Sodium thiosulfate	1.5 mg/mol Ag X
Chloroauric acid	1.0 mg/mol Ag X
Stabilizer (STAB-1)	6 × 10-4 mol/mol Ag X
Sensitizing dye (GS-1)	4 × 10-4 mol/mol Ag X

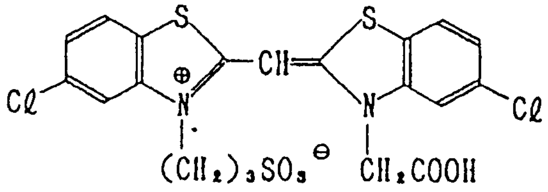
Preparation of red-sensitive silver halide emulsion

An monodispersed cubical silver halide emulsion, EM-3, was prepared in the same procedure as in EMP-1, except that the addition time of solutions A and B and that of solutions C and D were changed. EM-3 was comprised of grains having an average grain size of 0.50 μm, a grain size distribution variation coefficient (σ/r) of 0.08 and a silver chloride content of 99.5 mol%.

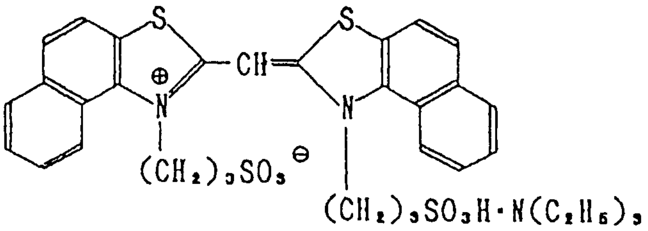
EMP-3 was chemically sensitized at 60 °C for 90 minutes using the following chemicals to obtain a red-sensitive silver halide emulsion, Em-R.

Sodium thiosulfate	1.8 mg/mol Ag X
Chloroauric acid	2.0 mg/mol Ag X
Stabilizer (STAB-1)	6×10^{-4} mol/mol Ag X
Sensitizing dye (BS-1)	4×10^{-4} mol/mol Ag X

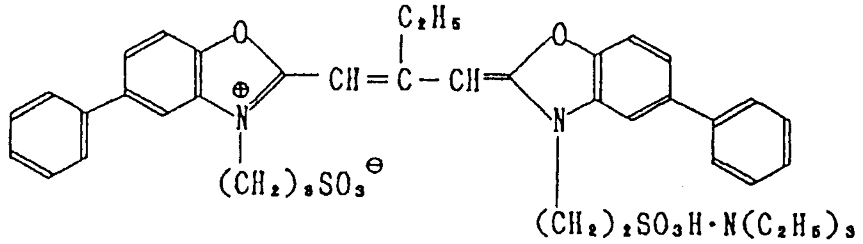
BS-1



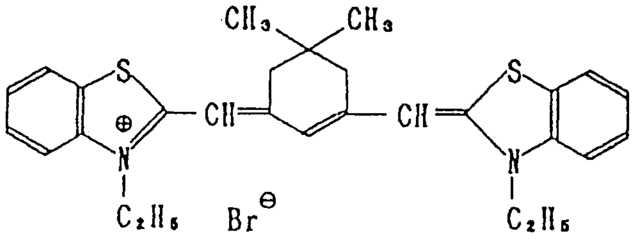
BS-2



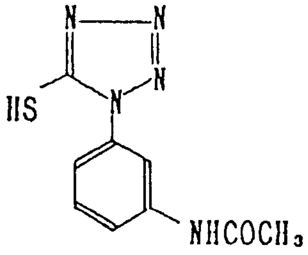
GS-1



RS-1



STAB-1



The light-sensitive material samples prepared as above were exposed according to a usual manner and processed by use of the following processes and processing solutions, then the waste processing solutions were reclaimed and recycled as described later.

Process

(1) Color developing	35.0 ± 0.3 °C	45 sec
(2) Bleach-fixing	35.0 ± 0.5 °C	45 sec
(3) Stabilizing (3 tanks, in cascade)	30 to 34 °C	90 sec
(4) Drying	60 to 80 °C	30 sec

Color developer tank solution

Triethanolamine	10 g
Ethylene glycol	6 g
N,N-diethylhydroxylamine	3.6 g
Hydrazinodiacetic acid	5.0 g
Potassium bromide	20 mg
Potassium chloride	2.5 g
Diethylenetriaminepentacetic acid	5 g
Potassium sulfite	5.0×10^{-4} mol
Developing agent [3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl-)aniline sulfate]	5.5 g
Potassium carbonate	25 g
Potassium hydrogencarbonate	5 g

Water is added to make 1 liter, then the pH is adjusted to 10.10 with potassium hydroxide or sulfuric acid.

Color developer solution replenisher

Triethanolamine	14.0 g
Ethylene glycol	8.0 g
N,N-diethylhydroxylamine	5 g
Hydrazinodiacetic acid	7.5 g
Potassium bromide	8 mg
Potassium chloride	0.3 g
Diethylenetriaminepentacetic acid	5.0 g
Potassium sulfite	7.0×10^{-4} mol
Developing agent [3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl-)aniline sulfate]	8 g
Potassium carbonate	30 g
Potassium hydrogencarbonate	1 g

Water is added to make 1 liter, then the pH is adjusted to 10.40 with potassium hydroxide or sulfuric acid.

Bleach-fixer tank solution and replenisher

Ammonium ferric ethylenediaminetetracetate	53.0 g
Ethylenediaminetetracetic acid	3.0 g
Ammonium thiosulfate (70% solution)	123.0 g
Ammonium sulfite (40% solution)	51.0 g

The pH is adjusted to 5.4 with aqueous ammonia or glacial acetic acid, and water is added to make 1 liter.

Stabilizer tank solution and replenisher

Ortho phenylphenol	0.15 g
Optical whitening agent (Uvitex made by Ciba Geigy)	1.0 g
$ZnSO_4 \cdot 7H_2O$	0.15 g
Ammonium sulfite (40% solution)	5.0 ml
1-Hydroxyethylidene-1,1-diphosphonic acid (60% solution)	2.5 g
Ethylenediaminetetracetic acid	1.5 g

The pH is adjusted to 7.8 with aqueous ammonia or sulfuric acid, and water is added to make 1 liter.

Using the color paper and the processing solutions prepared as above, processing was continuously run: firstly, an automatic processor was filled with the above color developer tank solution, bleach-fixer tank solution and stabilizer tank solution, and then the above color paper was continuously processed, during which the above color developer replenisher, bleach-fixer replenisher and stabilizer replenisher were fed thereto at 3-minute intervals through a volume measuring pump.

The amount replenished to the color developing tank was 100 ml per square meter of the color paper, that replenished to the bleach-fixing tank was 80 ml per square meter, and that replenished to the stabilizing tank was 250 ml per square meter.

This continuous processing was run at a rate of 0.05 R per day till the amount of the color developer replenisher fed to the color developing tank reached three times the volume of the color developer tank solution. Here, 1R means that the amount of the color developer replenisher fed reaches the capacity of the color developing tank.

After the continuous processing, a procedure to collect and recycling the overflow of the bleach-fixer tank was repeated three times. At that time, the surface tension was 43 dyn/cm and the silver ion concentration was 1.0×10^{-1} mol/l. After adjusting the pH of the above processing solution to 6.0 to 8.0, the compounds shown in Table 1 were added, followed by stirring for 1 minute. Next, a partially hydrolyzed polyacrylamide was added as a high-molecular flocculent, followed by stirring for 1 minute and filtration to remove the flocks. The filtrate was adjusted to pH 5.4 to reuse it as a bleach-fixer tank solution, with which the above exposed light-sensitive material was then processed under the above processing conditions.

In Table 1, the yellow stain was determined by measuring the blue light reflection density of the unexposed portion of the processed light-sensitive material using a PDA-65 made by Konica Corp.

ΔD_R, indicating fading of the cyan dye, was determined by steps of measuring the red light density at the maximum density portion of the processed light-sensitive material, dipping this light-sensitive material for 10 minutes at room temperature in a 100 g/l aqueous solution of $EDTAFeNH_4 \cdot 2H_2O$ adjusted to pH 6.0, rinsing it in running water for 5 minutes that followed by drying, measuring the red light density at the maximum density portion again, and subtracting the measured value before the Fe salt treatment from that after the treatment.

(Experiment 1)

For comparison, the above overflow was subjected to silver recovery for 1 hour at an electrolytic current of 18 A using a BN-10 made by Sun Seiki Seisakusho Co. and then reused as a bleach-fixer tank solution as it was, to process the light-sensitive material under the above conditions. The evaluation results are shown in Table 1.

Table 1

Compound added (1×10^{-1} mol/l)	Surface tension dyn/cm	Yellow stain	ΔD_R	Remarks
Silver recovery of (Experiment 1)	50	0.10	0.25	Comparison
$NaVO_3$ (solubility product: 5×10^{-7})	65	0.07	0.08	Invention
	60	0.03	0.03	
	55	0.02	0.02	
	40	0.01	0.01	
	30	0.02	0.03	
Sodium dithiocarbamate (solubility product: ca. 1×10^{-15} - 1×10^{-20})	65	0.02	0.02	Invention
	60	0.01	0.03	
	55	0.00	0.02	
	40	0.00	0.04	
	30	0.00	0.02	
$(CH_3)_2NCSSNa$ (solubility product: ca. 1×10^{-19})	65	0.02	0.02	Invention
	60	0.01	0.03	
	55	0.00	0.01	
	40	0.00	0.03	
	30	0.00	0.03	
$(C_2H_5)_2NCSSNa$ (solubility product: ca. 1×10^{-20})	40	0.00	0.03	Invention
Isopropyl mercaptan (solubility product: ca. 1×10^{-11} - 1×10^{-20})	40	0.00	0.03	Invention
Thioglycolic acid (solubility product: ca. 1×10^{-20})	40	0.00	0.01	Invention
Sodium sulfide (solubility product: ca. 1×10^{-40})	40	0.00	0.02	Invention
Thiourea (solubility product: ca. 1×10^{-20})	40	0.00	0.01	Invention
$NaBH_4$	65	0.02	0.03	Invention
	60	0.01	0.02	
	55	0.00	0.02	
	40	0.00	0.02	
	30	0.00	0.02	
$LiA1H_4$	40	0.00	0.02	Invention
Sodium hydrosulfite	40	0.00	0.02	Invention

It can be seen in Table 1 that use of the precipitant according to the invention reduces both of the formation of yellow stains and the fading of cyan dyes. Particularly, use of a precipitant having a solubility product not more than 1×10^{-9} produces much better results, and a recycling treatment at a surface tension not more than 60 dyn/cm is much more effective in preventing yellow stains.

Example 2

The following silver halide color photographic light-sensitive material was prepared.

Addition amounts of photographic components are in grams per square meter unless otherwise indicated. Amounts of silver halide and colloidal silver are shown in amounts of silver present.

A triacethylcellulose film support was subbed on one side, then the other side (backside) was coated with the following layers in sequence.

Backside 1st layer	
Alumina sol AS-100 (aluminium oxide made by Nissan Chemical Co.)	0.8 g

Backside 2nd layer	
Diacethylcellulose	100 mg
Stearic acid	10 mg
Silica fine particles (average size: 0.2 μm)	50 mg

Subsequently, the following layers were formed on the subbed side of the support in sequence to obtain a multilayered color photographic light-sensitive material (a-1).

1st layer: antihalation layer (HC)	
Black colloidal silver	0.15 g
UV absorbent (UV-1)	0.22 g
Colored cyan coupler (CC-1)	0.02 g
High boiling solvent (Oil-1)	0.20 g
High boiling solvent (Oil-2)	0.20 g
Gelatin	1.6 g

2nd layer: intermediate layer (IL-1)	
Gelatin	1.3 g

3rd layer: low-speed red-sensitive emulsion layer (R-L)	
Silver iodobromide emulsion (average grain size: 0.3 μm)	0.6 g
Silver iodobromide emulsion (average grain size: 0.4 μm)	0.3 g
Sensitizing dye (S-1)	3.2×10^{-4} (mol/Ag mol)
Sensitizing dye (S-2)	3.2×10^{-4} (mol/Ag mol)
Sensitizing dye (S-3)	$0.2 \times 10^{4-}$ (mol/Ag mol)
Cyan coupler (C-1)	0.50 g
Cyan coupler (C-2)	0.14 g
Colored cyan coupler (CC-1)	0.07 g
DIR compound (D-1)	0.006 g
DIR compound (D-2)	0.01 g
High boiling solvent (Oil-1)	0.55 g
Gelatin	1.0 g

4th layer: high-speed red-sensitive emulsion layer (R-H)	
Silver iodobromide emulsion (average grain size: 0.7 μm)	0.9 g
Sensitizing dye (S-1)	1.7×10^{-4} (mol/Ag mol)
Sensitizing dye (S-2)	1.7×10^{-4} (mol/Ag mol)
Sensitizing dye (S-3)	0.1×10^{-4} (mol/Ag mol)
Cyan coupler (C-2)	0.23 g
Colored cyan coupler (CC-1)	0.03 g
DIR compound (D-2)	0.02 g
High boiling solvent (Oil-1)	0.27 g
Gelatin	1.0 g

5th layer: intermediate layer (IL-2)	
Gelatin	0.8 g

6th layer: low-speed green-sensitive emulsion layer (G-L)	
Silver iodobromide emulsion (average grain size: 0.4 µm)	0.6 g
Silver iodobromide emulsion (average grain size: 0.3 µm)	0.2 g
Sensitizing dye (S-4)	6.7×10^{-4} (mol/Ag mol)
Sensitizing dye (S-5)	0.8×10^{-4} (mol/Ag mol)
Magenta coupler (M-1)	0.17 g
Magenta coupler (M-2)	0.44 g
Colored magenta coupler (CM-1)	0.10 g
DIR compound (D-3)	0.02 g
High boiling solvent (Oil-2)	0.7 g
Gelatin	1.0 g

7th layer: high-speed green-sensitive emulsion layer (G-H)	
Silver iodobromide emulsion (average grain size: 0.7 µm)	1.0 g
Sensitizing dye (S-6)	1.1×10^{-4} (mol/Ag mol)
Sensitizing dye (S-7)	2.0×10^{-4} (mol/Ag mol)
Sensitizing dye (S-8)	0.3×10^{-4} (mol/Ag mol)
Magenta coupler (M-1)	0.30 g
Magenta coupler (M-2)	0.13 g
Colored magenta coupler (CM-1)	0.04 g
DIR compound (D-3)	0.004 g
High boiling solvent (Oil-2)	0.35 g
Gelatin	1.0 g

8th layer: yellow filter layer (YC)	
Yellow colloidal silver	0.1 g
Additive (HS-1)	0.07 g
Additive (HS-2)	0.07 g
Additive (SC-1)	0.12 g
High boiling solvent (Oil-2)	0.16 g
Gelatin	1.0 g

9th layer: low-speed blue-sensitive emulsion layer (B-L)	
Silver iodobromide emulsion (average grain size: 0.3 µm)	0.25 g
Silver iodobromide emulsion (average grain size: 0.4 µm)	0.28 g
Sensitizing dye (S-9)	5.8×10^{-4} (mol/Ag mol)
Yellow coupler (Y-1)	0.6 g
Yellow coupler (Y-2)	0.32 g
DIR compound (D-1)	0.003 g
DIR compound (D-2)	0.006 g
High boiling solvent (Oil-2)	0.18 g
Gelatin	1.3 g

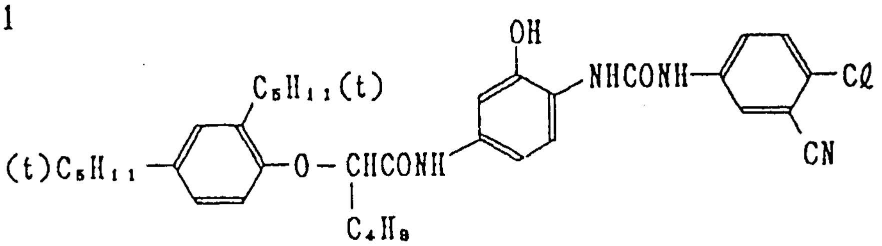
10th layer: high-speed blue-sensitive emulsion layer (B-H)	
Silver iodobromide emulsion (average grain size: 0.8 μm)	0.5 g
Sensitizing dye (S-10)	3×10^{-4} (mol/Ag mol)
Sensitizing dye (S-11)	1.2×10^{-4} (mol/Ag mol)
Yellow coupler (Y-1)	0.18 g
Yellow coupler (Y-2)	0.10 g
High boiling solvent (Oil-2)	0.05 g
Gelatin	1.0 g

11th layer: 1st protective layer (PRO-1)	
Silver iodobromide emulsion (average grain size: 0.08 μm)	0.3 g
UV absorbent (UV-1)	0.07 g
UV absorbent (UV-2)	0.12 g
Additive (HS-1)	0.2 g
Additive (HS-2)	0.1 g
High boiling solvent (Oil-1)	0.07 g
High boiling solvent (Oil-3)	0.07 g
Gelatin	0.8 g

12th layer: 2nd protective layer (PRO-2)	
Compound A	0.04 g
Compound B	0.004 g
Polymethylmethacrylate (average particle size: 3 μm)	0.02 g
Methyl methacrylate/ethyl methacrylate/methacrylic acid 3:3:4 (wt. ratio) copolymer (average particle size: 3 μm)	0.13 g

Besides the above components, the above color light-sensitive material further contains compounds Su-1 and Su-2, viscosity regulator, hardeners H-1 and H-2, stabilizer ST-1, antifoggants AF-1 and AF-2 (weight average molecular weights were 10,000 and 1,100,000, respectively), dyes AI-1 and AI-2, and compound DI-1 (9.4 mg/m^2).

C－1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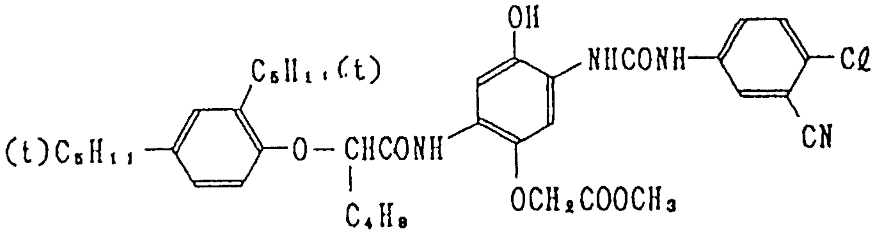
C－2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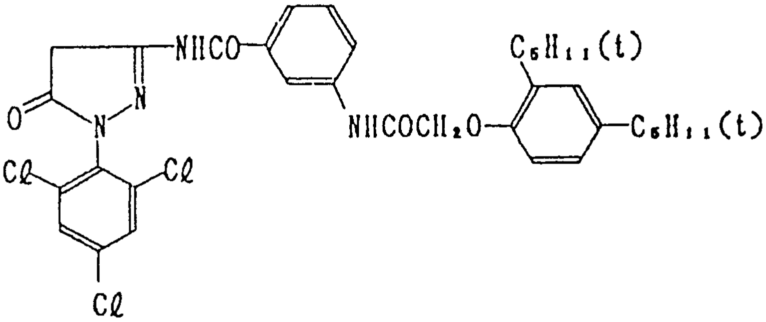
M－1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O
N
N
Cℓ
Cℓ
Cℓ
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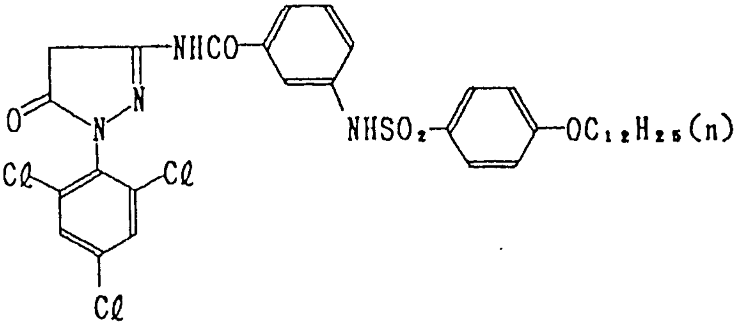
C₅H₁₁(t)

M－2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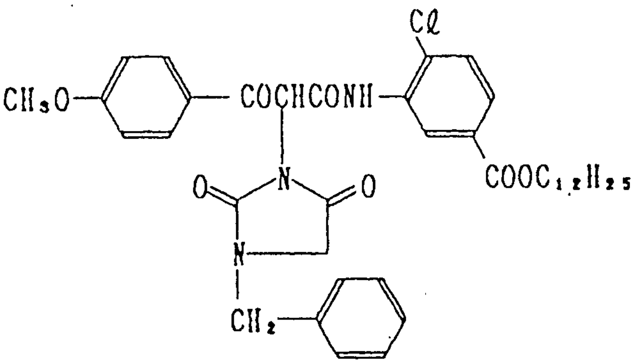
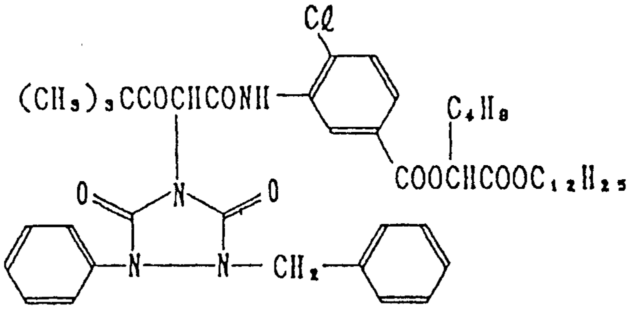
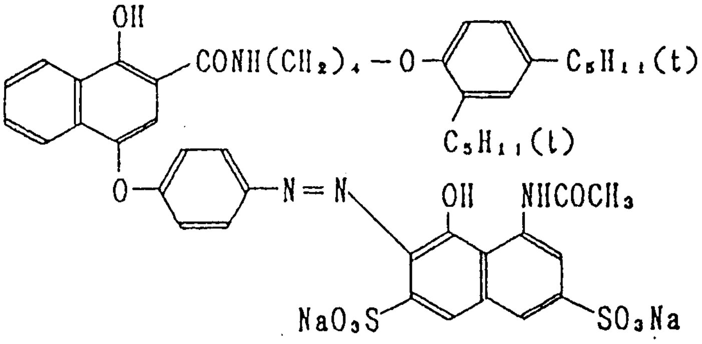
Y－1



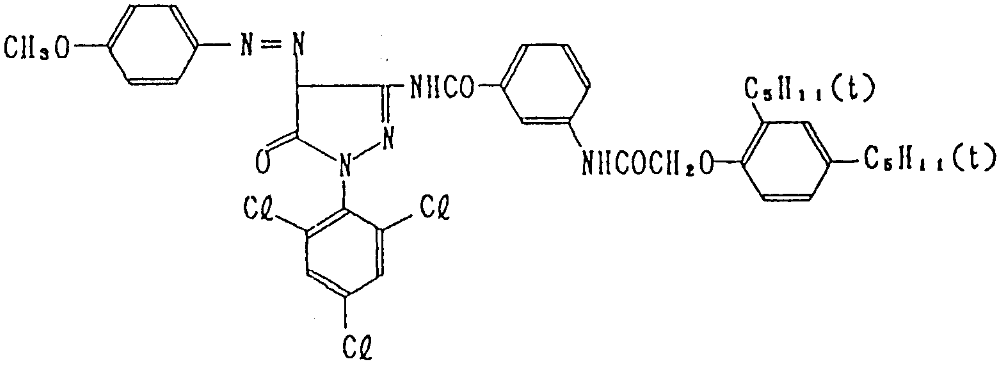
Y－2



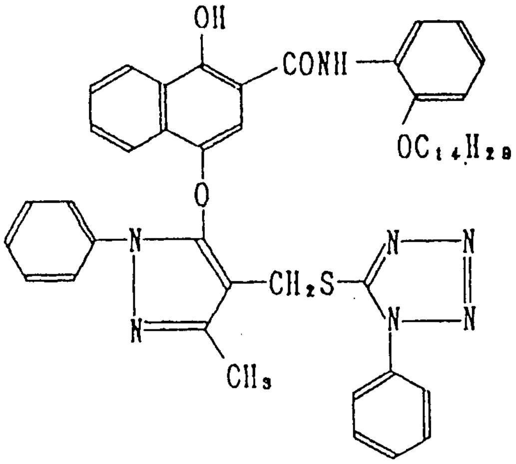
CC－1



CM－1



D－1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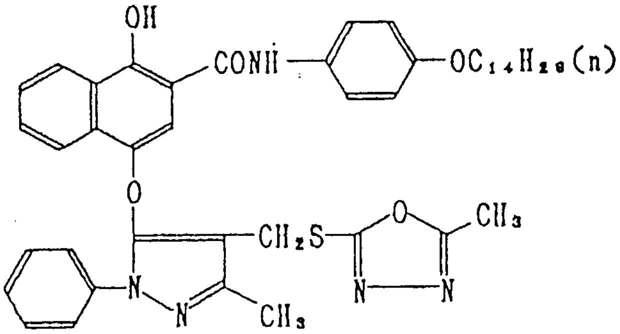
N
CH_2S
N
N
N
N
CH_3

D－2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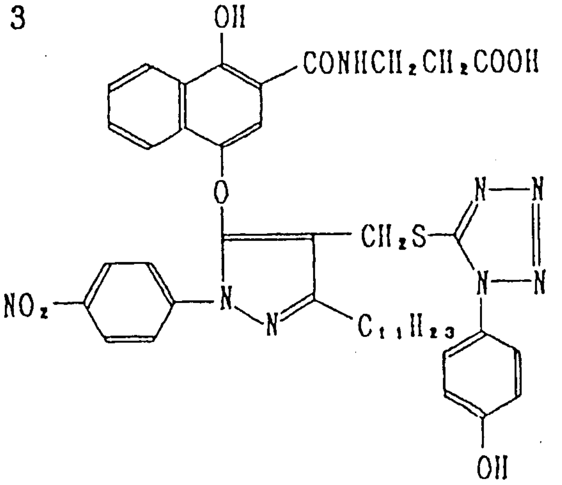
D－3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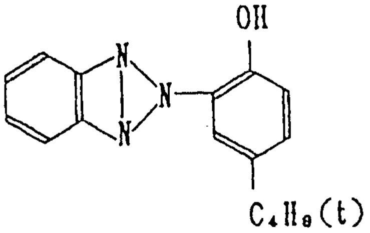
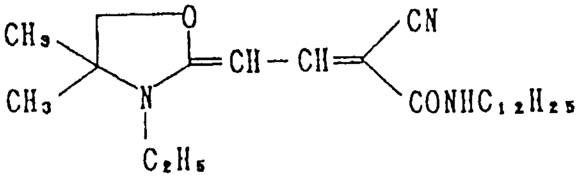
OH

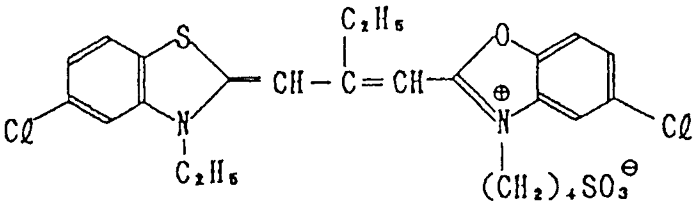
UV－1



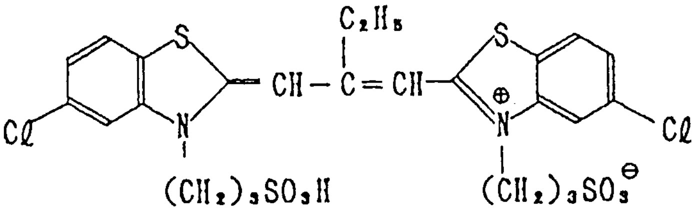
UV－2



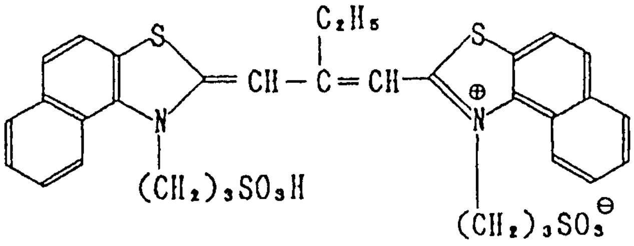
S－1



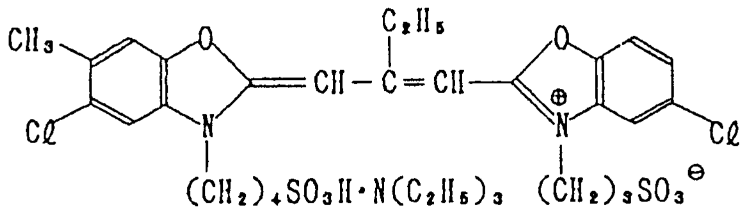
S－2



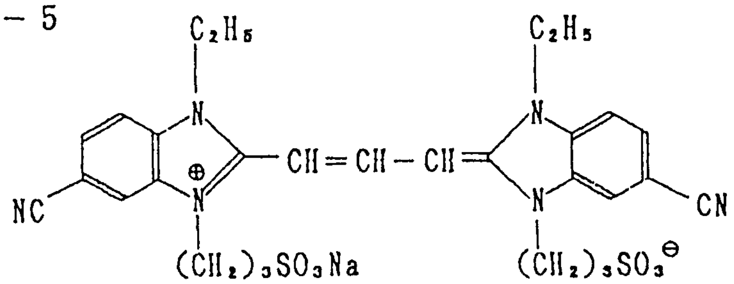
S－3



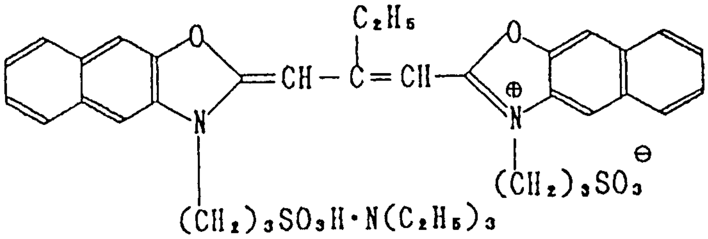
S - 4



S - 5



S - 6



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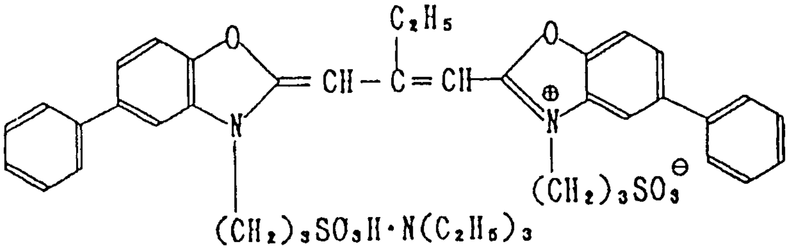

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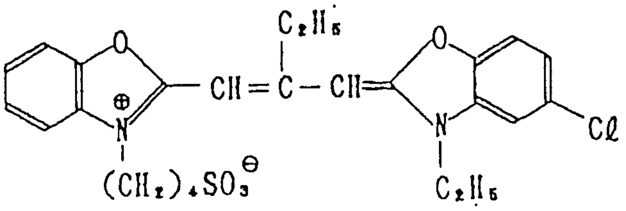
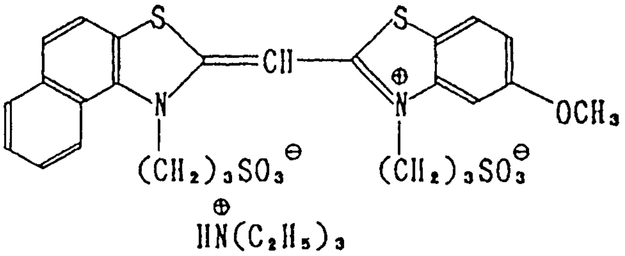
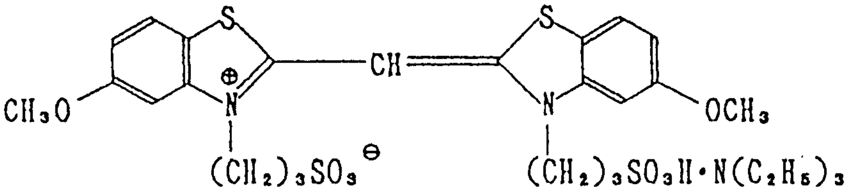


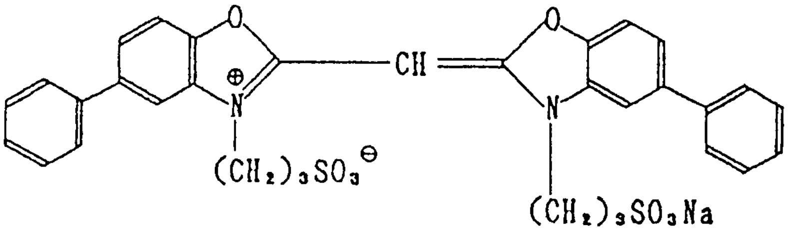
S − 9



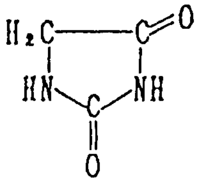
S − 10



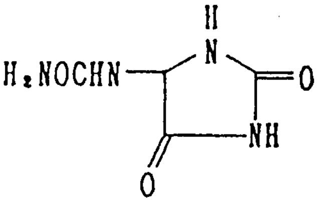
S − 11



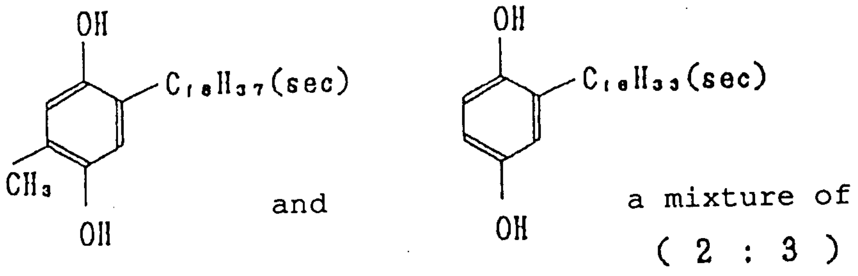
H S − 1



H S − 2

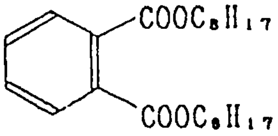


SC-1

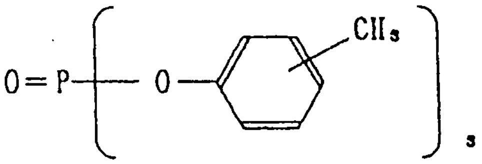


and a mixture of (2 : 3)

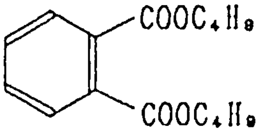
Oil-1



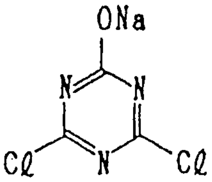
Oil-2



Oil-3



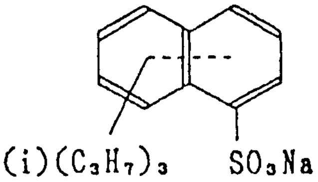
H-1



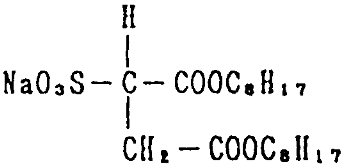
H-2

$(CH_2=CHSO_2CH_2)_2O$

SU-1

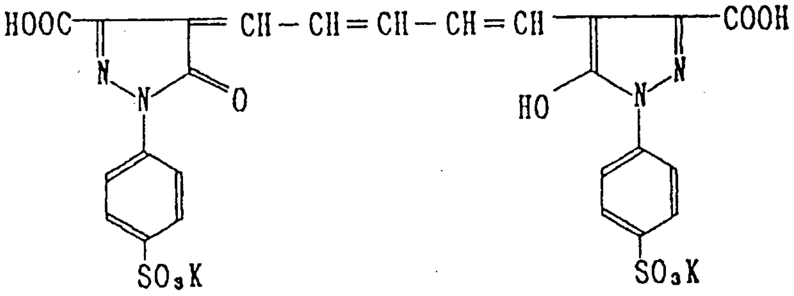


SU-2



$NaO_3S-\underset{CH_2-COOC_8H_{17}}{\overset{H}{C}}-COOC_8H_{17}$

A I − 1



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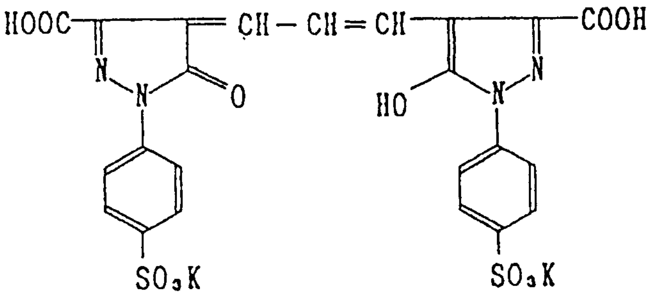
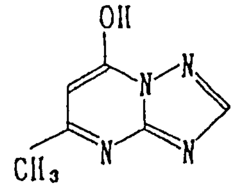
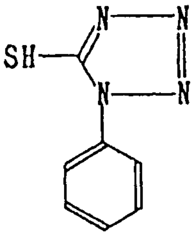


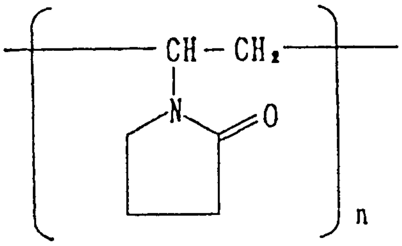
S T − 1



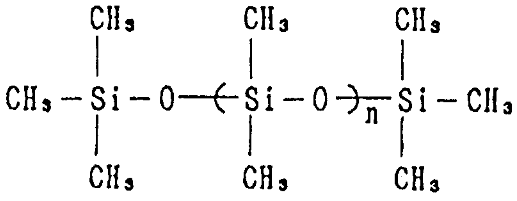
A F − 1



A F − 2



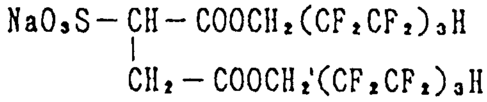
Compound A



$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-(\underset{CH_3}{\overset{CH_3}{Si}}-O)_n-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3}$$

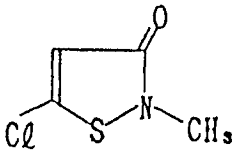
Weight average molecular weight = 30,000

Compound B

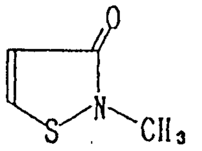


$$\begin{array}{l}\mathrm{NaO_3S-CH-COOCH_2(CF_2CF_2)_3H} \\ \qquad\quad | \\ \qquad\quad \mathrm{CH_2-COOCH_2(CF_2CF_2)_3H}\end{array}$$

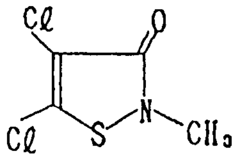
DI-1 (a mixture of the following three components)



component A



component B



component C

component A:component B:component C: = 50:46:40 (molar ratio)

[Preparation of emulsion]

The silver iodobromide emulsion used in the 10th layer was prepared by the double jet method, using monodispersed silver iodobromide grains with an average grain size of 0.33 μm and a silver iodide content of 2 mol% as seed grains.

Firstly, 0.34 mol equivalent of the seed emulsion was added with stirring to the following solution G-1 at 70 ° C, pAg 7.8 and pH 7.0.

Formation of internal high iodide content phase (core phase)

Then, the following solutions H-1 and S-1 were added thereto, keeping the flow ratio 1:1, over a period of 86 minutes at an accelerated flow (the final flow was 3.6 times as large as the initial flow).

Formation of outer low iodide content phase (shell phase)

While keeping the mother liquor pAg 10.1 and pH 6.0, solutions H-2 and S-2 were added at a flow ratio of 1:1 and at an accelerated flow (the final flow was 5.2 times as large as the initial flow) over a period of 65 minutes.

In the course of grain formation, the pAg and pH were controlled by use of a potassium bromide aqueous solution and a 56% acetic acid aqueous solution. After grains were formed, these were desalted by a conventional flocculation method, then dispersed again with the addition of gelatin, and the emulsion obtained was adjusted to pH 5.8 and pAg 8.06 at 40 ° C.

This emulsion was comprised of monodispersed octahedral silver iodobromide grains having an average grain size of 0.80 μm, a grain size distribution extent of 12.4%, and a silver iodide content of 8.5 mol.

Solution G-1	
Ossein gelatin	100.0 g
10% Methanol solution of compound-1	25.0 ml
28% Aqueous ammonia	440.0 ml
56% Acetic acid aqueous solution	660.0 ml
Water is added to make	5000.0 ml

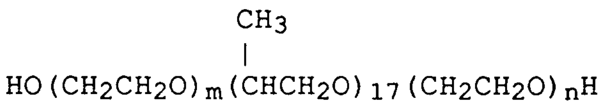
Solution H-1	
Ossein gelatin	82.4 g
Potassium bromide	151.6 g
Potassium iodide	90.6 g
Water is added to make	1030.5 ml

Solution S-1	
Silver nitrate	309.2 g
28% Aqueous ammonia	equivalent
Water is added to make	1030.5 ml

Solution H-2	
Ossein gelatin	302.1 g
Potassium bromide	770.0 g
Potassium iodide	33.2 g
Water is added to make	3776.8 ml

Solution S-2	
Silver nitrate	1133.0 g
28% Aqueous ammonia	equivalent
Water is added to make	3776.8 ml

Compound-1



$$HO(CH_2CH_2O)_m(\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2O)_{17}(CH_2CH_2O)_nH$$

Average molecular weight

The other emulsions different in average grain size and silver iodide content were prepared likewise by varying the average grain size of seed grains, temperature, pAg, pH, flow, addition time and halide composition.

Any of those emulsions was a monodispersed emulsion comprised of core/shell type grains having a grain size distribution extent less than 20%. Each emulsion was subjected to chemical ripening under optimum conditions in the presence of sodium thiosulfate, chloroauric acid and ammonium thiocyanate, and then sensitizing dyes, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 1-phenyl-5-mercaptotetrazole were added thereto.

The light-sensitive materials prepared as above, Gold 100 made by Eastman Kodak Co. and Super-HR-II100 made by Fuji Photo Film Co. were processed at a ratio of 2:1:2 using the following processes and processing solutions. The processing was continued for 1 month at a daily processing amount of 20 rolls (24 exposures) of film. Processing conditions

Process	Processing time	Processing temp	Amount (ml/m^2) replenished*
Color developing	3 min 15 sec	38 ° C	570
Bleaching	45 sec	38 ° C	155
Fixing	1 min 45 sec	38 ° C	500
Stabilizing**	1 min 30 sec	38 ° C	775
Drying	1 min	40 to 70 ° C	-

Notes * The amount replenished is shown by values per m^2 of light-sensitive material
** Stabilizing was performed in a 3-tank countercurrent system, in which the replenisher was fed to the final tank and the overflow was allowed to flow into the preceding tank.

Color developing solution

Potassium carbonate	30 g
Sodium hydrogencarbonate	2.7 g
Potassium iodide	1.2 mg
Potassium sulfite	2.8 g
Sodium bromide	1.3 g
Hydroxylamine sulfate	3.2 g
Sodium chloride	0.6 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl) aniline sulfate	4.6 g
Diethylenetriaminepentacetic acid	3.0 g
Potassium hydroxide	1.3 g

Water is added to make 1 liter, then the pH is adjusted to 10.01 with potassium hydroxide or 20% sulfuric acid.

Color developing replenisher

Potassium carbonate	40 g
Sodium hydrogencarbonate	3 g
Potassium sulfite	7 g
Sodium bromide	0.4 g
Hydroxylamine sulfate	3.2 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl) aniline sulfate	6.0 g
Diethylenetriaminepentacetic acid	3.0 g
Potassium hydroxide	2 g

Water is added to make 1 liter, then the pH is adjusted to 10.12 with potassium hydroxide or 20% sulfuric acid.

Bleaching solution

Ammonium ferric 1,3-diaminopropanetetracetate	0.35 mol
Disodium ethylenediaminetetracetate	2 g
Ammonium bromide	150 g
Glacial acetic acid	38 ml
Ammonium nitrate	40 g
Ammonium 1,3-diaminopropanetetracetate	2.0 g

Water is added to make 1 liter, then the pH is adjusted to 4.5 with aqueous ammonia or glacial acetic acid.

Bleaching replenisher

Ammonium ferric 1,3-diaminopropanetetracetate	0.40 mol
Disodium ethylenediaminetetracetate	2 g
Ammonium bromide	170 g
Ammonium 1,3-diaminopropanetetracetate	2.0 g
Ammonium nitrate	50 g
Glacial acetic acid	61 ml

Water is added to make 1 liter, then the pH is adjusted to 3.5 with aqueous ammonia or glacial acetic acid. The pH of the bleacher tank solution is kept constant by making adjustment as occasion demands.

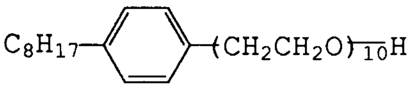
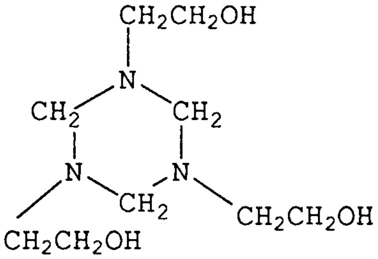
Fixing solution and replenisher

Ammonium thiosulfate	100 g
Ammonium thiocyanate	150 g
Anhydrous sodium bisulfite	20 g
Sodium metabisulfite	4.0 g
Disodium ethylenediaminetetracetate	1.0 g

Water is added to make 700 ml, and the pH is adjusted to 6.5 with glacial acetic acid or aqueous ammonia.

Stabilizing solution and replenisher

5-Chloro-2-methyl-4-isothiazoline-3-one	0.05 g
2-Methyl-4-isothiazoline-3-one	0.02 g

	2.0 ml
Hexamethylenetetramine	0.5 g
	0.3 g

Water is added to make 1 liter, and the pH is adjusted to 7.0 with potassium hydroxide or 50 % sulfuric acid.

Each sample was subjected to continuous processing in the same manner as in Example 1. Then, the fixing solution was processed and evaluated in the same manner as in Example 1. In the evaluation, the blue light density at the unexposed portion was determined by subtracting the mask density. The evaluation results were much the same as those obtained in Example 1.

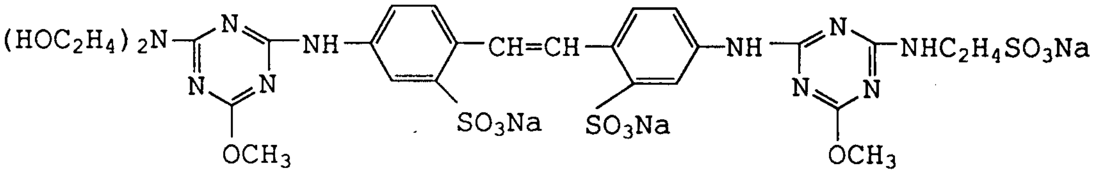
Example 3

The same procedure as in Example 1 was repeated, except that 1 g/l of an optical whitening agent was contained in the bleach-fixing solution to evaluate the effect of preventing yellow stains.

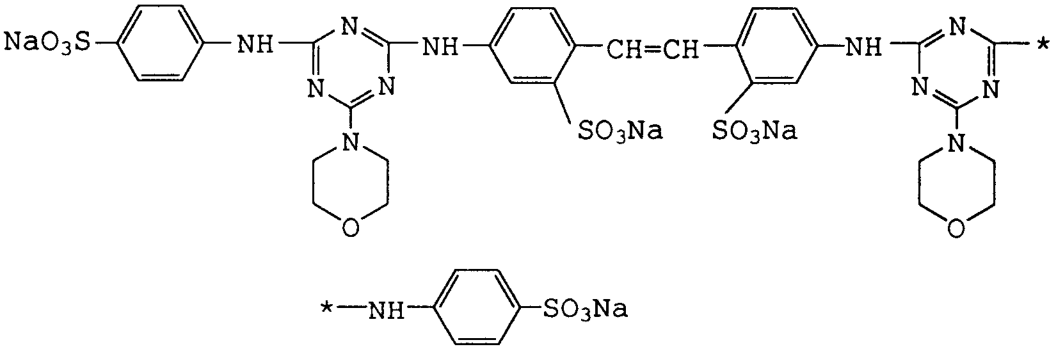
The results showed that the formation of yellow stains could be reduced by 5 to 20%.

As the optical whitening agent, the following E-4, E-24, E-34, E-35, E-36 and E-44 were used.

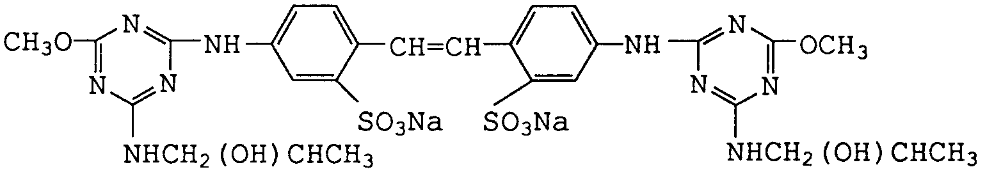
(E-4)



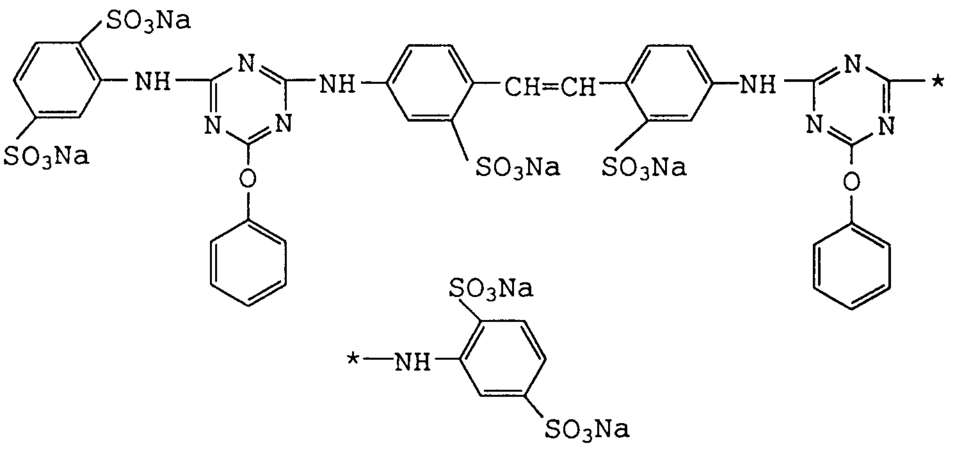
(E-24)



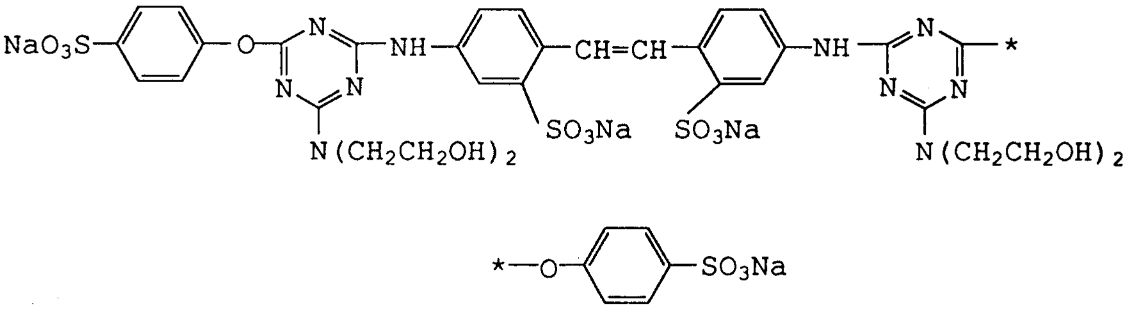
(E-34)



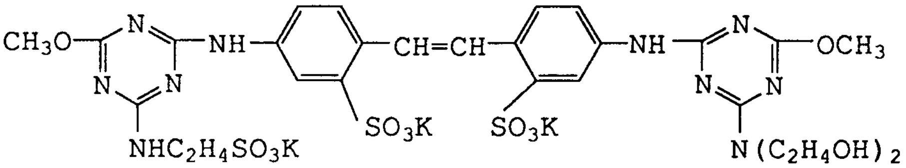
(E-35)



(E-36)



(E-44)



Example 4

The procedure of Example 2 was repeated, except that the ammonium thiosulfate in the fixing solution was replaced by sodium thiosulfate of the same molar concentration, and that the ammonium thiocyanate was also replaced by potassium thiocyanate of the same molar concentration. The results are shown in Table 2.

Table 2

Compound added (1×10^{-1} mol/l)	Surface tension (dyn/cm)	Transmitted blue light density at unexposed portion after subtracting mask density
$NaVO_3$ (solubility product: 5×10^{-7})	65 60 55 40 30	0.11 0.09 0.04 0.02 0.02
Sodium dithiocarbamate (solubility product: ca. 1×10^{-15} - 1×10^{-20}	65 60 55 40 30	0.06 0.03 0.02 0.01 0.01
$(CH_3)_2NCSSNa$ (solubility product: ca. 1×10^{-19})	65 60 55 40 30	0.07 0.04 0.03 0.01 0.01
$(C_2H_5)_2NCSSNa$ (solubility product: ca. 1×10^{-20})	40	0.01
Isopropyl mercaptan (solubility product: ca. 1×10^{-11} - 1×10^{-20})	40	0.01
Thioglycolic acid (solubility product: ca. 1×10^{-20})	40	0.02
Sodium sulfide (solubility product: ca. 1×10^{-40})	40	0.01
Thiourea (solubility product: ca. 1×10^{-20})	40	0.00
$NaBH_4$	65 60 55 40 30	0.06 0.04 0.01 0.01 0.01
$LiA1H_4$	40	0.02
Sodium hydrosulfite	40	0.02

It can be understood from the table that the formation of yellow stains in the samples of Table 2 is less than that in the samples of Table 1, this indicates that the reduction in ammonium ion content is effective in preventing the formation of yellow stains.

Example 5

The following emulsion A was prepared.

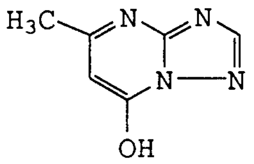
(Emulsion A)

Solution 1	Gelatin Water	20 g 400 ml
Solution 2	$AgNO_3$ Water Aqueous ammonia (28%)	70 g 250 ml 40 ml
Solution 3	KBr Water	42 g 300 ml
Solution 4	0.5% $K_2[Ir(IV)Cl_6]$ Water	0.75 ml 36.68 ml

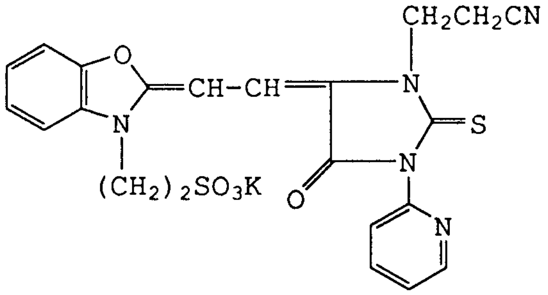
There was pipetted 0.25 ml of solution 4 and added to solution 1 (the addition amount of iridium salt was 2.9×10^{-7} mol/mol Ag X). Solution 1 was heated to 35 ° C, and then solutions 2 and 3 were simultaneously added thereto in 1 minute with vigorous stirring. The liquor was ripened for 5 minutes at that temperature and adjusted to pH 5.8 with 20% acetic acid, then the temperature was raised to 40 ° C. After desalting by use of Demol N (product of Kao Co.) and magnesium sulfate, the resulting emulsion was dispersed again by adding gelatin. Emulsion A so obtained was comprised of monodispersed cubical grains having an average grain size of 0.3 μm.

Emulsion A was subjected to chemical sensitization under optimum conditions using sodium thiosulfate. After stopping the chemical sensitization by adding the following inhibitor SB-1, the emulsion was subjected to spectral sensitization under optimum conditions using the following sensitizing dyes A and B.

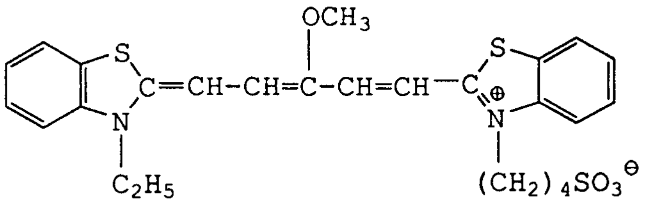
Inhibitor SB-1



Sensitizing dye A

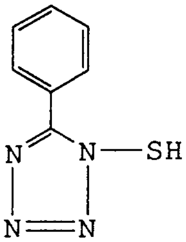
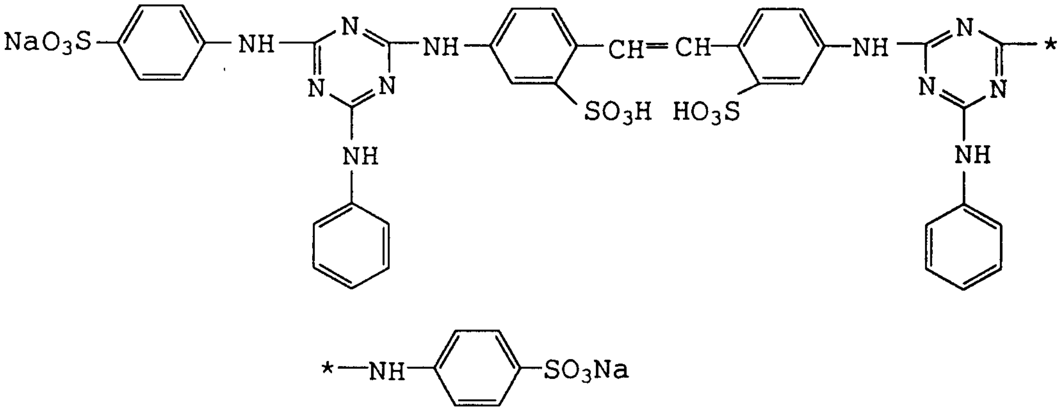


Sensitizing dye B

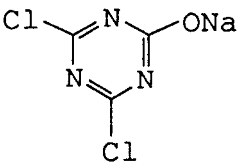


Next, a light-sensitive material sample was prepared by simultaneously coating the following emulsion layer and protective layer on a 200-μm thick paper support laminated with polyethylene on both sides.

(Emulsion layer)

Binder: gelatin	2.8 g/m^2
Emulsion above (in terms of silver)	1.4 g/m^2
Toning agent: 	10 mg/m^2
Optical whitening agent: 	10 mg/m^2
Coating aid: sodium dodecylbenzenesulfonate	50 mg/m^2

(Protective layer)

Binder: gelatin	1.5 g/m^2
Coating aid: sodium dodecylbenzenesulfonate	50 mg/m^2
	0.1 g/m^2

Each sample was wedgewise exposed and then processed according to the following processes.

Process	Temperature	Time		Amount replenished
Developing	33 °C		45 sec	200 ml/m^2
Fixing	31 °C		45 sec	200 ml/m^2
Stabilizing	31 °C	1st tank	30 sec*	250 ml/m^2
		2nd tank	30 sec	
		3rd tank	30 sec	
Drying	50 to 70 °C		70 sec	-

* A 3-tank countercurrent system was used by feeding a replenisher to the 3rd tank.

Developer tank solution

Phenidone	0.2 g
Potassium sulfite (anhydrous)	70 g
Hydroquinone	7.1 g
Disodium ethylenediaminetetracetate	0.6 g
Sodium carbonate	7.0 g
Boric acid (anhydrous)	3.5 g
Acetic acid (90%)	1.2 g
Potassium bromide	5 g
Benzotriazole	20 mg
Caustic soda	4 g

Water is added to make 1 liter, and the pH is adjusted to 10.2 with acetic acid and caustic soda.

Developer replenisher

Potassium sulfite (anhydrous)	70 g
Hydroquinone	7.1 g
Disodium ethylenediaminetetracetate	0.6 g
Phenidone	0.2 g
Sodium carbonate	7.0 g
Boric acid (anhydrous)	3.5 g
Benzotriazole	20 mg
Potassium bromide	2.5 g
Caustic soda	4 g

Water is added to make 1 liter, and the pH is adjusted to 10.5 with acetic acid and caustic soda.

Fixing tank solution and replenisher

Ammonium thiosulfate (73%)	210 g
Sodium sulfite	20 g
Boric acid (anhydrous)	6 g
Sodium acetate	20 g
Acetic acid (90%)	7 g
Aluminium sulfate	11 g
Conc. sulfuric acid (98%)	1 g

Water is added to make 1 liter, and the pH is adjusted to 5.0 with sulfuric acid and aqueous ammonia.

Stabilizer tank solution and replenisher

Potassium sulfite	0.3 g
Ammonium sulfite	6.0 g
Potassium hydroxide (48.55%)	0.1 g
Ethylenediaminetetracetatic acid	1.5 g

Water is added to make 1 liter, and the pH is adjusted to 8.0 with sulfuric acid and aqueous ammonia.

Continuous processing was performed until the amount of replenisher reached three times as that of tank solution.

After completion of the continuous processing, the fixing solution was recycled as in Example 1, and the formation of yellow stains was observed. The results are shown in Table 3

As apparent from Table 3, the results were much the same as in Example 1 and the formation of yellow stains was limited to a small extent.

Table 3

Compound added ($1x10^{-1}$ mol/l)	Surface tension dyn/cm	Yellow stain	Remarks
Silver recovery of (Experiment 1)	50	0.05	Comparison
$NaVO_3$ (solubility product: 5×10^{-7})	65	0.03	Invention
	60	0.02	
	55	0.01	
	40	0.01	
	30	0.01	
Sodium dithiocarbamate (solubility product: ca. 1×10^{-15} - 1×10^{-20})	65	0.01	Invention
	60	0.01	
	55	0.00	
	40	0.00	
	30	0.00	
$(CH_3)_2NCSSNa$ (solubility product: ca. 1×10^{-19})	65	0.01	Invention
	60	0.01	
	55	0.00	
	40	0.00	
	30	0.00	
$(C_2H_5)_2NCSSNa$ (solubility product: ca. 1×10^{-20})	40	0.00	Invention
Isopropyl mercaptan (solubility product: ca. 1×10^{-11} - 1×10^{-20})	40	0.00	Invention
Thioglycolic acid (solubility product: ca. 1×10^{-20})	40	0.00	Invention
Sodium sulfide (solubility product: ca. 1×10^{-40})	40	0.00	Invention
Thiourea (solubility product: ca. 1×10^{-20})	40	0.00	Invention
$NaBH_4$	65	0.01	Invention
	60	0.00	
	55	0.00	
	40	0.00	
	30	0.00	
$LiA1H_4$	40	0.00	Invention
Sodium hydrosulfite	40	0.00	Invention

Claims

1. A process of recycling a processing solution of a silver halide photographic light-sensitive material comprising a support and provided thereon, a silver halide emulsion layer, comprising the steps of;
   processing the material with the processing solution, precipitating a silver compound in the processing solution using a precipitant,
   removing the precipitated silver compound to regenerate the solution, and
   recycling the solution.

2. The process of claim 1, wherein said processing solution is a solution having a fixing capability.

3. The process of claim 1, wherein said precipitant is a compound of which the solubility product with silver ion is not more than 10^{-9}.

4. The process of claim 2, wherein said precipitant is a compound of which the solubility product with silver ion is not more than 10^{-9}.

5. The process of claim 3, wherein said compound is selected from tetrazaindene derivatives, 6-aminopurine derivatives, and sulfur compounds.

6. The process of claim 4, wherein said compound is selected from tetrazaindene derivatives, 6-aminopurine derivatives, and sulfur compounds.

7. The process of claim 1, wherein said precipitating is carried out using a precipitant and a flocculant.

8. The process of claim 1, wherein said precipitating is carried out using a precipitant and a reducing agent.

9. The process of claim 8, wherein said reducing agent is selected from the group consisting of boron hydride salts, aluminium hydride salts and hydrosulfites.

10. The process of claim 2, wherein the surface tension of said solution is not more than 60 dyn/cm.

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	FERNSEH UND KINO TECHNIK. vol. 38, no. 9, September 1984, BERLIN DE pages 369 - 376; GERHARD BERGFRIED: 'Neue Recycling-Verfahren in der Filmentwicklung' * page 369, column 2 * ---	1,2	G03C5/395 G03C7/44
X	DD-A-204 169 (H-U GALGON ET AL) * the whole document * ---	1,2,8,9	
X	US-A-3 832 453 (I.SLOVONSKY ET AL) * the whole document * ---	1-4	
X Y	FR-A-2 189 776 (ILFORD LIMITED) * page 1, line 24 - line 39 * ---	1-6 7,10	
X	DE-A-2 041 128 (AGFA-GEVAERT AKTIENGESELLSCHAFT) * page 3, paragraph 2 - page 4, paragraph 1 * ---	1-6	
Y	JOURNAL OF APPLIED PHOTOGRAPHIC ENGINEERING. vol. 5, no. 3, 1979, SPRINGFIELD US pages 144 - 147; M.M.COOK ET AL: 'Use of sodium borohydride to control heavy metal discharge in the photographic industry' * page 146, right column, line 6 - page 147, line 4 * ---	7	TECHNICAL FIELDS SEARCHED (Int. Cl.5) G03C
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 AUGUST 1992	BOLGER W.

CATEGORY OF CITED DOCUMENTS

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