



EUROPEAN PATENT APPLICATION

Application number: **90113278.7**

Int. Cl.⁵: **G03C 5/395, G03C 7/44**

Date of filing: **11.07.90**

Priority: **20.07.89 JP 186135/89**

Date of publication of application:
23.01.91 Bulletin 91/04

Designated Contracting States:
BE DE FR GB IT NL

Applicant: **FUJI PHOTO FILM CO., LTD.**
210 Nakanuma Minami Ashigara-shi
Kanagawa(JP)

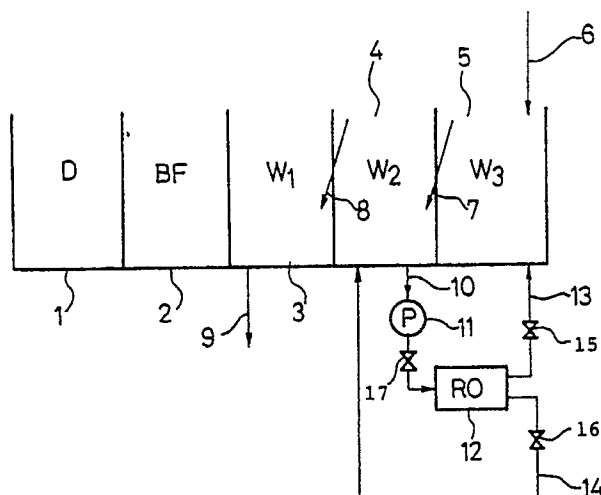
Inventor: **Abe, Akira**
c/o Fuji Photo Film Co., Ltd., No. 210,
Nakanuma
Minami, Ashigara-shi, Kanagawa(JP)

Representative: **Patentanwälte Grünecker,**
Kinkeldey, Stockmair & Partnerner
Maximilianstrasse 58
D-8000 München 22(DE)

A method of processing silver halide photographic materials.

A method of processing silver halide photographic materials is described which includes processing an imagewise-exposed silver halide photographic material in a bath which has a fixing ability and then processing the photographic material in at least one of a water washing bath and a stabilizing bath, wherein at least one of washing water and stabilizing solution from at least one of the water washing bath and the stabilizing bath, respectively, is subjected to a reverse osmosis treatment using a reverse osmosis membrane which removes NaCl in a amount of 30% to 90% when treating a 1000 ppm NaCl solution at 25 °C under a feed pressure of 7 kg/cm².

FIGURE 1



A METHOD OF PROCESSING SILVER HALIDE PHOTOGRAPHIC MATERIALSFIELD OF THE INVENTION

5 This invention concerns a method of processing silver halide photographic materials, and in particular it concerns a method of processing silver halide photographic materials in such a way that the washing water and/or stabilizing bath is regenerated by a reverse osmosis membrane treatment.

BACKGROUND OF THE INVENTION

10

After imagewise exposure, silver halide color photographic materials are subjected to processes such as color development, bleach-fixing and water washing.

15 Silver halide color reversal photographic materials are subjected to black-and-white development processing prior to color development. Furthermore, black-and-white silver halide photographic materials are, after imagewise exposure, subjected to processes such as black-and-white development, fixing and water washing.

20 In recent years, a demand has arisen for minimizing the hazardous components in effluent streams and reducing the amount of effluent, or providing a system with no effluent. In particular, from the viewpoints of environmental protection and conservation of resources, a demand has arisen for a reduction in the amount of washing water. Various studies have been conducted in response to these demands.

Ion exchange resin methods (see J. Appl. Phot. Eng. , 6 , 120 (1980) and *ibid* , 5 , 141 (1979)) and reverse osmotic pressure apparatus (see Soviet Union Patent 701,963) are known in connection with the reuse of washing water.

25 Among these methods, improvements have been made in the techniques by which washing water is subjected to a reverse osmosis treatment. One such type of improved color photographic processing apparatus is furnished with a reverse osmotic pressure device in which the solution intake, the concentrate side outlet and the diluted side output are connected to a water washing tank, the bleach-fix tank and the water washing tank respectively. The washing water expelled from the water washing tank is treated by
30 means of the reverse osmotic pressure device, and the concentrate which is produced is returned to the bleach-fix tank while the dilute solution is returned to the water washing tank (JP-A-58-105150). (The term "JP-A" as used herein signifies an "unexamined published Japanese patent application".)

35 Furthermore, JP-A-60-241053 describes a method of processing in which silver halide color photographic materials are color developed, processed in a processing bath which has a fixing capacity and then subjected to a stabilizing process essentially without water washing, wherein the stabilizer solution is treated by means of a reverse osmosis membrane. With this method of processing, the production of yellow staining on long term storage and the development of staining immediately after processing are said to be prevented.

40 Moreover, JP-A-62-254151 describes a method of processing silver halide color photographic materials in which, when water washing and/or stabilizing is carried out using a multi-stage counter-flow system after processing a silver halide color photographic material in a bath which has a fixing function, the overflow from the water washing tank and/or stabilizing tank is introduced into a storage tank, and the solution in the storage tank is treated with a reverse osmosis membrane. The solution permeating through the reverse osmosis membrane returns to the water washing tank and/or the stabilizing tank, and the concentrated
45 solution returns to the storage tank in order to reduce the amount of concentrated solution which is expelled from the reverse osmosis membrane treatment apparatus and to minimize replenishment of the washing water. The amount of water used in the washing and/or stabilizing process can be greatly reduced when this method is used, and the processing can be accomplished without increased yellow staining even though the amount of water which is being used is reduced.

50 The reverse osmosis membrane treatment of washing water and stabilizing solution is very useful for greatly reducing amount of washing water or stabilizing solution.

A problem which arises on reducing the amount of washing water or stabilizing solution, especially in color processing, is that the concentration of aminopolycarboxylic acid ferric complex salts, for example EDTA-Fe, increases in the water or solution in the water washing tank or stabilizing tank due carry-over from the bath which has a fixing ability and which contains the aminopolycarboxylic acid ferric complex salt,

and the concentration increases in the final bath particular. There is a particular problem with increased yellow staining of the processed photosensitive material when the concentration in the final bath exceeds 0.0003 mol/liter. Furthermore, silver contamination of the photosensitive material due to the formation of silver sulfide, for example, also occurs because of an increased silver concentration in the final bath.

5 The methods of processing described above all involve reusing the expelled washing water or expelled stabilizing solution by means of a reverse osmosis treatment and are such that uncontaminated washing water or stabilizing solution is obtained. An effective reverse osmosis membrane which produces washing water or stabilizing solution which is of high purity can be used for the reverse osmosis membrane treatment. With the treatment apparatus described in JP-A-58-105150 in particular, the valuable components
10 in the washing water are recovered and returned to the bleach-fixing tank, so a reverse osmosis membrane of the type which passes virtually no solute is used. Reverse osmosis membranes of this type have fine pores, so the operating pressure is high. In fact, the operating pressure in the treatment apparatus described in the JP-A-58-105150 is from 40 to 50 kg/cm², and the operating pressure in the method of treatment described in JP-A-60-241053 where stabilizing solution is being subjected to a reverse osmosis
15 membrane treatment is 55 kg/cm².

As a result of research into methods of processing silver halide color photographic materials in which a reverse osmosis membrane treatment is incorporated, the inventors discovered that very little yellow staining occurred when the EDTA-Fe was completely removed in the reverse osmosis membrane treatment.

Thus, the fact that the occurrence of yellow staining is suppressed with the method of processing
20 described in JP-A-60-241053 can be explained by the fact that the solute (EDTA-Fe) is completely removed with the use of a reverse osmosis membrane which has a high operating pressure as described earlier. The suppression of yellow staining in the method of processing described in JP-A-62-254151 is accomplished in the same way. A reverse osmosis membrane which has fine pores is used such that virtually all of the solute is removed in the way described above in these methods of processing.

25 Expelled washing water or stabilizing solution can be reused to a high degree when reverse osmosis membranes which have such fine pores are used. However, with such a high degree of reuse, when silver halide color photographic materials are washed, for example, in water or solution- from which all the salts, etc. have been removed, the problem of reticulation occurs depending on changes in humidity in storage after processing. This produces fine crinkly wrinkles in the surface of the emulsion film and results in a
30 dulling of the luster. Consequently, the image quality is greatly reduced. Moreover, an increase in the extent of cyan dye fading is another adverse effect.

On investigating the cause of these effects and countermeasures, it was found that the effects resulted from the fact that the emulsion layer had become susceptible to pronounced swelling from humidity because of a very low salt content in the washing water and that a small residue of NH₄ ion, K ion, and Na
35 ion in the permeated water in the reverse osmosis membrane treatment was advantageous for stopping the occurrence of reticulation and increasing image stability. The NH₄ ion, K ion and Na ion originate from the carry-over of the ammonium thiosulfate, etc. from the bath in which bleaching or bleach-fixing is being carried out.

40

SUMMARY OF THE INVENTION

45 The aim of the present invention is to provide a method of processing silver halide color photographic materials with a sufficiently high rate of water permeation in which the EDTA-Fe which is the cause of yellow staining is completely removed while a small residual NH₄ salt content is maintained in the permeated water.

Thus, the present invention is a method of processing silver halide photographic materials which includes processing an imagewise-exposed silver halide photographic material in a bath which has a fixing
50 ability and then processing the photographic material in at least one of a water washing bath and stabilizing bath, wherein at least one of washing water and stabilizing solution from at the least one of the water washing bath and the stabilizing bath, respectively, is subjected to a reverse osmosis treatment using a reverse osmosis membrane which removes NaCl in an amount of 30% to 90% when treating a 1000 ppm NaCl solution at 25 °C under a feed pressure of 7 kg/cm².

55

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram of the processing apparatus as used in Example 1, and Figure 2 is a diagram of the processing apparatus as used in Example 2, both of which are described below, wherein:

- 1 and 21 are color development tanks (D); 2 is a bleach-fixing tank (BF);
- 3 and 25 are first water washing tanks (W_1);
- 5 4 and 26 are second water washing tanks (W_2);
- 5 and 27 are third water washing tanks (W_3);
- 6 and 29 are washing water; 7, 8, 30, 31 and 38 are connecting pipes; 9, 32, and 39 are overflow streams,
- 10 and 33 are flow pipes for removing washing water; 11 and 34 are pumps (P);
- 12 and 35 are reverse osmosis membrane module;
- 10 13, 14, 36 and 37 are connecting pipes; 15, 16 and 17 are valves;
- 22 is a bleach tank (B);
- 23 is a first fixing tank (F_1);
- 24 is a second fixing tank (F_2); and
- 28 is a stabilizing tank (S);

15

DETAILED DESCRIPTION OF THE INVENTION

20 This method of processing is especially effective for the processing of silver halide color photographic materials where a color development process and a bleaching process are involved.

Reverse osmosis membranes which have various fine pore sizes have permeation characteristics which are based on the fine pores. However, it is difficult to measure precisely the pore structure, such as the porosity, of a membrane. Even when measurements as to what can be permeated have been made, it is
25 impossible to make comparisons where the substances used have differed. Most recently, the characteristics of reverse osmosis membranes have been represented by the extent of the removal of NaCl on permeating an NaCl solution and this has come to be used as a standard. There is some correlation between the amount of NaCl removed and the state of the fine pores of a membrane.

The present invention, uses a reverse osmosis membrane which removes NaCl in an amount of about
30 30% to about 90% under conditions such as those described earlier. Those membranes which remove NaCl in an amount of from about 40% to about 85% are preferred, and those which remove NaCl in an amount of from about 50% to about 80% are especially desirable. Also, those membranes which remove EDTA-Fe(III) in an amount at least 90% are preferred. In the treatment of the developed color photographic material, the solution of a final water wash tank or stabilizing tank contains not more than 0.0003 mol/l of
35 EDTA-Fe(III), preferably not more than 0.0002 mol/l and the most preferably not more than 0.0001 mol/l.

On the other hand, a concentration of ammonium salt in permeated water is preferably from 6.7×10^{-4} to 3.4×10^{-3} mol/l.

Actual examples of such reverse osmosis membranes include DRA-40, DRA-80 and DRA-89 made by the Daicell Chemical Co., and of these DRA-80 is especially desirable.

40 These reverse osmosis membranes are composed of a porous polysulfone film as a substrate to which an aromatic polyamide film of 0.2 μ m in thickness having anionic charge are intimately attached as a separating film. The membranes having such a constitution as above is called as a composite film.

A NaCl removal of DRA-40, DRA-80 and DRA-89 is about 45%, about 80% and about 85% respectively, when 1000 ppm of aqueous NaCl solution is fed under pressure of 7 kg/cm².

45 Since these membranes are made of polymer, the membranes show superior anti-bacteria properties comparing with those made of cellulose acetate which are liable to be suffered from bacterial. In view of the foregoing, these membranes are remarkably advantageous in regenerating a waste solution in photographic processings.

SU-200 membrane is also made of aromatic polyamide separating film and polysulfone substrate and
50 shows NaCl removal of about 60% which is made by the Toray Co.

Suitable reverse osmosis membranes, include cellulose acetate membranes, ethyl cellulose/polyacrylic acid membranes, polyacrylonitrile membranes, poly(vinylene carbonate) membranes, polyether-based membranes, crosslinked aramid-based composite membranes, and crosslinked polyamide-based composite membranes.

55 The composite membrane is composed of a porous polymer substrate, with which a thin polymer film having solute separating function is integrated. Preferable composite membrane according to the present invention includes those having a substrate of porous polysulfone film which is reinforced with polyester non-woven fabric, and a polymer thin film formed by plasma polymerization or interfacial polymerization,

preferably with further effective crosslinking reaction.

Example of the thin film includes aromatic polyamide and aromatic polyimide, having 0.1 to 0.4 μm in thickness, preferably 0.15 to 0.25 μm .

Reverse osmosis membranes with a spiral, tubular, hollow fiber, pleated or rod type construction can be used. The membrane may be a single layer membrane or a plural membrane, but plural membranes (synthetic plural membranes) are preferred from the viewpoint of durability with respect to EDTA-Fe.

These reverse osmosis membranes are comprised of a skin layer which dominates membrane performance characteristics such as the amount of water permeated and the removal rates, for example, and a supporting layer which supports the skin layer. There are asymmetrical membranes in which the two are comprised of the same material and composite membranes in which they are comprised of different materials. Examples of asymmetrical membranes include cellulose acetate membranes, and examples of composite membranes include synthetic composite membranes in which a skin layer is formed by coating polyethyleneimine and tolylenediisocyanate onto a supporting layer of polysulfone and those in which a skin layer is formed by polymerizing furfuryl alcohol. Details of synthetic composite membranes have been disclosed in The Development and Practical Use of High Separation Techniques, pages 155 - 172, special edition 29 - 7 of Kagaku Kogyo, published by the Kagaku Kogyo Co. The use of these composite membranes is preferred in the present invention in view of their removal rates, water permeation rates and EDTA-Fe durability.

Moreover, the reverse osmosis membranes used in reverse osmosis membrane treatments carried out in the past removed NaCl in an amount of at least 95%. These membranes completely removed the solutes referred to earlier rather than allowing them to be present. Membranes which remove NaCl in an amount of at least 95% must be operated under a high pressure to obtain a practical water permeation rate. With the reverse osmosis membranes according to the present invention (which remove NaCl in amounts of about 30% to about 90%), a sufficiently high water permeation rate can be achieved at a pressure of from 2 to 10 kg/cm², but with the reverse osmosis membrane DRA-98 (which removes NaCl in an amount of 98%), a similar water permeation rate cannot be realized without a pressure of at least 15 kg/cm². According to the present invention, the water permeation is preferably carried out under a pressure of from 3 to 7 kg/cm², more preferably from 3 to 5 kg/m² in consideration of reducing a running cost, power consumption, noises pollution, and heat generation.

In the case where four washing tanks or stabilization tanks are present, the preferred position for the removal of washing water or stabilizing solution from the water washing process or the stabilization process for reverse osmosis treatment is from the third tank, and the permeated water which has been subjected to reverse osmosis for reuse is supplied to the fourth stage, to which fresh water or solution is also being supplied. Washing water or stabilizing solution can also be removed from any of the water washing tanks or stabilizing tanks, or from two or more of these tanks.

The water washing process or the stabilization process is preferable carried out in multiple stages, preferably in 3 to 5 stages, the more preferably 3 to 4 stages. In the multiple stages process, a solution is preferably passed through under a counter flow.

Various compounds may be added to the washing water or stabilizing solution in the present invention. For example, film hardening agents as typified by magnesium salts and aluminum salts, surfactants for reducing the drying load and preventing unevenness, fluorescent whiteners for improving whiteness and sulfites as preservatives may be added. Alternatively, the compounds disclosed in, for example, L.E. West, "Water Quality Criteria", Photo. Sci. and Eng., Volume 9, No. 6 (1965), may be added.

In the present invention, a stabilizing solution is a solution which has an image stabilizing function which cannot be achieved with water washing. Such a solution contains components which fulfill an image stabilizing role in addition to the aforementioned components which can be added to the washing water.

For example, it may be a solution to which formalin, bismuth salts and aqueous ammonia or ammonium salts, for example, have been added.

The pH of the washing water or stabilizing solution in the present invention is generally about 7, but it may be within the range from 3 to 9, depending on the carry-over from the previous bath. The water washing or stabilization temperature is generally from 5°C to 40°C, and preferably from 10°C to 35°C. Heaters, temperature controllers, circulating pumps, filters, floating lids and squeegees, etc. may be used, in the water washing tanks or stabilizing tanks.

The processing method of the present invention is effective when applied to cases in which the concentration of aminopolycarboxylic acid ferric complex salt increases in the final water wash tank or stabilizing tank because of a reduced replenishment rate in which the rate of replenishment of the washing water or stabilizing solution is not more than 200 ml/m². Further, the rate of replenishment is preferably from 50 to 190 ml/m² when three water wash tanks or stabilizing tanks may be used, and is also preferably from

50 to 120 ml/m² when four water wash tanks or stabilizing tanks may be used.

The development processing of the photographic materials in the present invention may be processing in which a silver image is formed (black-and-white processing) or it may involve a development process in which a colore image is formed (color development processing). In those cases where an image is formed using a reversal procedure, a black-and-white negative development process is carried out first, followed by a white light exposure or treatment in a bath which contains a fogging agent, and a color development process.

Black-and-white development processing consists of a development process, a fixing process and a water washing process. A stop process is sometimes carried out after the development process, and in cases where a stabilizing process is carried out after the fixing process, the water washing process can be omitted. Development processes in which lith developers are used for the developer can also be used.

The known black-and-white developers generally used for the processing of black-and-white photographic materials can be used for the black-and-white developer which is used for the black-and-white processing operation, and the various additives which are generally added to a black-and-white developer can be included.

Typical additives include developing agents such as 1-phenyl-3-pyrazolidone, metol and hydroquinone, preservatives such as sulfites, accelerators comprised of alkalis such as sodium hydroxide, sodium carbonate and potassium carbonate, inorganic or organic restrainers such as potassium bromide or 2-methylbenzimidazole and methylbenzthiazole, water softening agents such as polyphosphate, and surface super-development inhibitors such as trace quantities of iodide or mercapto compounds.

Color development processing is carried out with a color development process, a bleaching process, a fixing process, a water washing process and, where required, a stabilizing process, but a bleach-fixing process with a single bleach-fix bath can be used instead of processing with a process in which a bleach bath is used and a process in which a fixing bath is used. Mono-bath processing in which a single developing, bleaching and fixing bath is used for color development, bleaching and fixing, can also be used.

Pre-film hardening processes, and neutralizing processes, stop-fix processes and post-film hardening processes, for example, can be combined with these processes.

Typical color development processing procedures for the present invention are indicated below, but processing is not limited to the examples shown.

- A. Color development - bleach-fix - water wash - dry
- B. Color development - bleach-fix - water wash -stabilization - dry
- C. Color development - water wash - bleach-fix - water wash - dry
- D. Color development - bleach-fix - water wash -stabilization - dry
- E. Color development - bleach-fix - water wash - dry
- F. Color development - water wash - bleach-fix - water wash - dry
- G. Color development - bleach - bleach-fix - water wash -stabilization - dry
- H. Color development - bleach - bleach-fix - water wash -dry
- I. Color development - bleach - bleach-fix - fix - water wash - stabilization - dry
- J. Color development - bleach - bleach-fix - fix - water wash - dry

In the above examples where process prior to the stabilization process is a water washing process, this water washing process can be omitted and the stabilization process can be carried out directly.

A color developing agent is present in the color development baths which are used in the present invention. The p-phenylene diamines derivatives are preferred and typical examples are indicated below, but the developing agent is not limited by these examples.

- D-1 N,N-Diethyl-p-phenylenediamine
- D-2 2-Amino-5-diethylaminotoluene
- D-3 2-Amino-5-(N-ethyl-N-laurylamino)toluene
- D-4 4-[N-Ethyl-N-(β -hydroxyethyl)amino]aniline
- D-5 2-Methyl-4-[N-ethyl-N-(β -hydroxyethyl)amino]aniline
- D-6 N-Ethyl-N-(β -methanesulfonamidoethyl)-3-methyl-4-aminoaniline
- D-7 N-(2-Amino-5-diethylaminophenylethyl)methanesulfonamide
- D-8 N,N-Diethyl-p-phenylenediamine
- D-9 4-Amino-3-methyl-N-ethyl-N-methoxyethylaniline
- D-10 4-Amino-3-methyl-N-ethyl-N- β -ethoxyethylaniline
- D-11 4-Amino-3-methyl-N-ethyl-N- β -butoxyethylaniline

Furthermore, these p-phenylenediamine derivatives may take the form of salts, such as their sulfates, hydrochlorides, sulfites and p-toluenesulfonates. The compounds indicated above have been disclosed, for example, in U.S. Patents 2,193,015, 2,552,241, 2,566,271, 2,592,364, 3,656,950 and 3,698,525. The primary

aromatic amine developing agents are used at concentrations of from about 0.1 gram to about 20 grams, and preferably from about 0.5 gram to about 10 grams, per liter of developer.

Known hydroxylamines can be present in the color development baths which are used in the present invention.

5 Although hydroxylamines can be used in a color development bath in the form of the free amines, they are more generally used in the form of their water soluble salts. General examples of such salts include the sulfates, oxalates, chlorides, phosphates, carbonates and acetates. The hydroxylamines may be substituted or unsubstituted, and the nitrogen atoms of the hydroxylamines may be substituted with alkyl groups.

The color development baths used in this present invention preferably have a pH of from 9 to 12, and
10 most desirably have a pH of from 9 to 11.0.

Other compounds already known as development bath components can also be used in the color development bath. For example, caustic soda, caustic potash, sodium carbonate, potassium carbonate, sodium tertiary phosphate, potassium tertiary phosphate, potassium metaborate and borax can be used either individually or in combinations as alkalis and pH buffers. Furthermore, various salts, such as disodium
15 or dipotassium hydrogen phosphate, potassium or sodium dihydrogen phosphate, sodium or potassium carbonate, boric acid, alkali nitrate or alkali sulfate, for example, can be used to provide a buffering capacity, for mixing purposes or for increasing the ionic strength.

Various chelating agents can be used to prevent the precipitation of calcium or magnesium in the color development bath. Examples of suitable chelating agents include polyphosphates, amino-polycarboxylic
20 acids, phosphonocarboxylic acids, amino-polysulfonic acids and 1-hydroxy-alkylidene-1,1-diphosphonic acids.

Optional development accelerators can be added to the color development baths, where required. Suitable development accelerators include various pyridinium compounds and other cationic compounds as typified by those disclosed in U.S. Patent 2,648,604, JP-B-44-9503 and U.S. Patent 3,171,247, neutral salts
25 such as thallium nitrate and potassium nitrate, non-ionic compounds such as the polyethyleneglycol, derivatives thereof and polythiol ethers disclosed, for example, in JP-B-44-9304 and U.S. Patents 2,533,990, 2,531,832, 2,950,970 and 2,577,127, and the thioether-based compounds disclosed in U.S. Patent 3,201,242. (The term "JP-B" as used herein signifies an "examined Japanese patent publication")

Furthermore, sodium sulfite, potassium sulfite, potassium bisulfite and sodium bisulfite, which are
30 generally used as preservatives, can be added.

Optional anti-foggants can be added, where required, to the color development bath in the present invention. Alkali metal halides, such as potassium bromide, sodium bromide and potassium iodide, and organic anti-foggants can be used as anti-foggants. Suitable examples of organic anti-foggants include nitrogen-containing heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 5-nitroisindazole,
35 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chlorobenzotriazole, 2-thiazolylbenzimidazole, 2-thiazolylmethylbenzimidazole and hydroxyazaindolizine, mercapto-substituted heterocyclic compounds such as 1-phenyl-5-mercaptotetrazole, 2-mercaptobenzimidazole and 2-mercaptobenzthiazole, and mercapto-substituted aromatic compounds such as thiosalicylic acid can be used. The nitrogen-containing heterocyclic compounds are especially desirable. These anti-foggants may be dissolved out of the color photosensitive material
40 during processing and accumulated in the color development bath.

Iron complexes are included among the bleaching agents in the bleach baths or bleach-fix baths which can be used in the present invention. The aminopolycarboxylic acid iron complexes are preferred from among the iron complexes and are added in an amount of from 0.01 to 1.0 mol/liter, and preferably in an amount of from 0.05 to 0.50 mol/liter.

45 Thiosulfate can be used as a fixing agent in the fixing baths or bleach-fixing baths. Ammonium thiosulfate is especially desirable and can be added in an amount of from 0.1 to 5.0 mol/liter, and preferably in an amount of from 0.5 to 2.0 mol/liter.

Sulfite is generally added in the fixing or bleach-fixing bath as a preservative, but ascorbic acid, carbonyl/bisulfite adducts or carbonyl compounds can also be used for this purpose. Moreover, buffers,
50 fluorescent whiteners, chelating agents and fungicides, for example, can also be added, in the fixing or bleach-fixing bath where required.

Various compounds can be used as bleaching accelerators in the bleach baths, bleach-fix baths and/or bleach or bleach-fix pre-baths. For example, the compounds which have a mercapto group or a disulfide group disclosed in U.S. Patent 3,893,858, West German Patent 1,290,812, JP-A-53-95630 and Research
55 Disclosure, No. 17129 (July, 1978), the thiazolidine derivatives disclosed in JP-A-50-140129, the thiourea derivatives disclosed in U.S. Patent 3,706,561, the iodide disclosed in JP-A-58-16235, the polyethyleneoxides disclosed in West German Patent 2,748,430 and the polyamine compounds disclosed in JP-B-45-8836 can be used for this purpose.

The photographic material to which the invention is applied may be, for example, an ordinary black-and-white silver halide photographic material (for example, a camera black-and-white sensitive material, an X-ray black-and-white sensitive material or a black-and-white sensitive material for printing purposes), an ordinary multi-layer color photosensitive material (for example, a color negative film, a color reversal film, a color positive film, a color negative film for cinematographic purposes), or a sensitive material for use with infrared light laser scanners.

No particular limitation is imposed upon the type of silver halide used, the method of manufacture, the method of chemical sensitization, the anti-foggants, stabilizers, film hardening agents, anti-static agents, couplers, plasticizers, lubricants, coating promoters, matting agents, whiteners, spectral sensitizers, dyes and ultraviolet absorbers which are used in the silver halide emulsion layers and surface protective layers, for example, or the support of the photographic material in the present invention. In this regard, one can refer to the disclosures, for example, in Product Licensing, Volume 92, pages 107 - 110 (December, 1971), Research Disclosure, No. 17643 (December, 1978), ibid, No. 18176 (November, 1979) and ibid, No. 23815 (February, 1984).

Color development processing using a color development process is effective for the efficient realization of the present invention and is the preferred type of processing in the present invention.

The couplers preferably used in the color photosensitive materials in the present invention are described below.

The couplers disclosed, for example, in 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 European Patent 249,473A are preferred as yellow couplers.

5-Pyrazolone-based compounds and pyrazoloazole-based compounds are preferred as magenta couplers, and those disclosed, for example, in U.S. Patents 4,310,619 and 4,351,897, European Patent 73,636, U.S. Patents 3,061,432 and 3,725,064, 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, JP-A-60-185951, U.S. Patents 4,500,630, 4,540,654 and 4,556,630, and WO(PCT) 88/04795 are especially desirable.

Phenol-based couplers and naphthol-based couplers are used as cyan couplers, and those disclosed, for example, in 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, 4,334,011 and 4,327,173, West German Laid-Open Patent 3,329,729, European Patents 121,365A and 249,453A, U.S. Patents 3,446,622, 4,333,999, 4,753,871, 4,451,559, 4,427,767, 4,690,889, 4,254,212 and 4,296,199, and JP-A-61-42658 are preferred.

The colored couplers for correcting the unwanted absorptions of colored dyes disclosed, for example, in section VII-G of Research Disclosure, No. 17643 (December, 1978), 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 are preferred. Furthermore, the use of couplers which correct the unwanted absorption of colored dyes by means of fluorescent dyes which are released on coupling as disclosed in U.S. Patent 4,774,181 is desirable.

The couplers disclosed in U.S. Patent 4,366,237, British Patent 2,125,570, European Patent 96,570 and West German Laid-Open Patent 3,234,533 are preferred as couplers which release colored dyes having a suitable degree of diffusibility.

Typical examples of polymerized dye-forming couplers have been disclosed, for example, in U.S. Patents 3,451,820, 4,080,211, 4,367,282, 4,409,320 and 4,576,910, and British Patent 2,102,173.

The use of couplers which release photographically useful residual groups on coupling is preferred in the present invention. The DIR couplers which release development inhibitors disclosed in the patents cited in section VII-F of the Research Disclosure 17643 (December, 1978), JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, JP-A-63-37346 and U.S. Patent 4,248,962 are preferred.

The couplers disclosed in British Patents 2,097,140 and 2,131,188, JP-A-59-157638 and JP-A-59-170840 are preferred as couplers which release nucleating agents or development accelerators in the form of the image during development.

Other couplers which can be used in the photosensitive materials in the present invention include the competitive couplers disclosed, for example, in U.S. Patent 4,130,427, the multi-equivalent couplers disclosed, for example, in U.S. Patents 4,283,472, 4,338,393 and 4,310,618, the DIR redox compound-releasing couplers, DIR coupler-releasing couplers, DIR coupler-releasing redox compounds or DIR redox-releasing redox compounds disclosed, for example, in JP-A-60-185950 and JP-A-62-24252, the couplers disclosed in European Patent 173,302A, which release dyes which have had their color restored after elimination, the bleach accelerator-releasing couplers disclosed, for example, in Research Disclosure No. 11449, ibid, No. 24241, and JP-A-61-201247, the ligand releasing couplers disclosed, for example, in U.S. Patent 4,553,477, the leuco dye releasing couplers disclosed in JP-A-63-75747, and the couplers disclosed

in U.S. Patent 4,774,181, which release fluorescent dyes.

It has been found in the present invention that when, in a method of processing silver halide color photographic materials, a reverse osmosis membrane having a 30% to 90% NaCl removal rate for a 1000 ppm NaCl solution being passed at 25° C at a pressure of 7 kg/cm² is used for the reverse osmosis membrane treatment of the washing water and/or stabilizing solution, the aminopolycarboxylic acids and thiosulfate/silver complex salts which cause problems are removed in amounts of at least 95% and that there is no increase in reticulation or fading of the cyan dye.

The precise reason for this is unclear in technological terms, but it is conjectured that a suitable quantity of univalent ions, such as ammonium, potassium or sodium ions for example, remains in the permeated water in a reverse osmosis treatment in which such a membrane is used, and that this quantity of ions suppresses variations in the film properties on drying due to the swelling of the films in the photosensitive material and suppresses the film pH after processing.

Furthermore, the reverse osmosis membranes used in the reverse osmosis membrane treatment in the present invention have a lower NaCl removal rate than those used conventionally, so the operating pressure can be reduced, the pump generates less heat and there is no problem with a rising solution temperature.

The invention is described in practical terms below by means of examples, but the invention is not limited to these examples. Unless otherwise indicated, all parts, percents, ratios and the like are by weight.

20

EXAMPLE 1

The color printing paper described below was cut to a width of 82.5 mm, exposed in an automatic printer and then processed on the basis of the processing operations indicated in Table 1 under the processing conditions described below in a processing apparatus which had water washing tanks to which a reverse osmosis membrane module was attached, as shown in Figure 1. Three days after processing, the processed color printing paper samples were assessed in regard to (1) reticulation which had occurred on storage, (2) fading of the cyan dye, and (3) adhesion between prints.

30

Processing Apparatus

In Figure 1, 1 is the color development tank (D), 2 is the bleach-fix tank (BF), and 3, 4 and 5 are the first water washing tank W₁, the second water washing tank W₂ and the third water washing tank W₃, respectively. Fresh washing water 6 is supplied to the third water washing tank (W₃) 5, and washing water from this tank is fed via the connecting pipe 7 to the second water washing tank (W₂) 4 of the previous stage, and ultimately via the connecting pipe 8 to the first water washing tank (W₁) 3, thereby providing a multi-stage counter-flow system.

Washing water was taken out via the connecting pipe 10 from the second water washing tank (W₂) 4 and fed by the pump (P) 11 to the reverse osmosis membrane module (RO) 12. The permeated water obtained from the reverse osmosis membrane module 12 was supplied to the third water washing tank (W₃) 5 via the connecting pipe 13 and the concentrate was returned to the second water washing tank (W₂) 4 via the connecting pipe 14.

Reverse osmosis membranes for the reverse osmosis membrane module 12 were selected from among the synthetic composite membranes of the DRA series and the cellulose acetate membranes of the DRC series made by the Daicell Chemical Co., and from among the composite membranes of the SU-200 series made by the Toray Co. The membranes removed NaCl in amounts as estimated using the method described below.

Amount of NaCl Removed: The value indicated below obtained on supplying an aqueous NaCl solution containing 1000 mg/liter of NaCl at 25° C at a pressure of 7 kg/cm².

55

$$\frac{1000 - \text{NaCl in Permeated Water (mg/l)}}{1000} \times 100 (\%)$$

The operating conditions were as follows. The reverse osmosis pressure due to the pump (P) 11 and

the openings of the valves 15, 16 and 17 were adjusted in such a way as to maintain a washing water flow rate from the water washing tank (W_2) 4 to the reverse osmosis membrane module (RO) 12 of 3 liters/minute and a permeated water flow rate from the reverse osmosis membrane module 12 of from 150 to 200 ml/min. The actual pressure was within the range from 3 to 12 kg/cm². The tempered circulation of the automatic developing machine was run for 10 hours per day, and the reverse osmosis membrane device was operated continuously during this time.

Color developer, bleach-fixer and water washing water having the compositions described below were supplied to the color development tank (D) 1, the bleach-fix tank (BF) 2 and the first to the third water washing tanks (W_1 - W_3) 3 - 5 of this processing apparatus.

The processing operations in the processing apparatus were as shown in Table 1.

15

20

25

30

35

40

45

50

55

Table 1 -Processing Operations

Process	Temperature	Processing Time	Tank Capacity	Replenishment Rate
Color Development	38°C	40 seconds	8 liters	65 ml/m ²
Bleach-fix	38°C	40 seconds	8 liters	60 ml/m ²
Water Wash (1)	38°C	18 seconds	4 liters	Three stage
Water Wash (2)	38°C	18 seconds	4 liters	counter-flow
Water Wash (3)	38°C	18 seconds	4 liters	108 ml/m ²
Drying	80°C	45 seconds		

5	<u>Color Developer</u>		<u>Mother Solution</u>	<u>Replenisher</u>
	Ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid		3.0 grams	4.0 grams
	Triethanolamine		4.0 grams	8.0 grams
	Sodium chloride		3.5 grams	-
10	Potassium bromide		0.01 gram	-
	N,N-bis(carboxymethyl)hydrazine		5.0 grams	10.0 grams
	Fluorescent whitener (4,4'-diaminostilbene-based)		1.0 gram	1.5 grams
15	Potassium carbonate		6.5 grams	28.0 grams
	N-Ethyl-N-(β -methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate		5.5 grams	10.0 grams
20	Potassium hydroxide	to	pH 10.05	pH 10.20
	Water	to make up to	1 liter	1 liter

25

30

35

40

45

50

55

<u>Bleach-Fixer</u>		<u>Mother solution</u>	<u>Replenisher</u>
Ammonium thiosulfate solution (700 g/l)		100 ml	200 ml
Ammonium sulfite		10 grams	25 grams
Ethylene diamine tetra-acetic acid, ferric ammonium salt, di-hydrate		55 grams	110 grams
Ethylenediamine tetra-acetic acid, di-sodium salt, dihydrate		3 grams	6 grams
Ammonium bromide		35 grams	20 grams
Glacial acetic acid	to	pH 5.5	pH 4.3
Water	to make up to	1 liter	1 liter

Washing Water

5

Chlorinated sodium isocyanurate (10 mg/l) was added to town water having a calcium content of 27 mg/l, a magnesium content of 4.2 mg/l, a pH of 7.3 and an electrical conductivity of 183 $\mu\text{S}/\text{cm}$.

10 Methods of Evaluation

Reticulation Occurring on Storage:

15 The processed samples were left to stand for 2 days under conditions of 25 °C and 55% relative humidity, after which they were moved to an environment at 25 °C and 90% relative humidity, and the presence and extent, or absence, of reticulation of the emulsion film surface was observed.

20 Fading of the Cyan Dye:

Samples which had been given a 250 CMS wedge exposure at a color temperature of 2854K and processed were stored for 3 weeks under conditions of 80 °C and 70% relative humidity, and the change in the maximum density region of the cyan dye was expressed as a percentage.

25

Adhesion Properties:

30 Printing papers (3.5 cm x 3.5 cm) which had been subjected to a full exposure and processed were left to stand for 2 days under conditions of 25 °C and 80% relative humidity. After the samples were placed together with the emulsion surfaces facing one another, they were loaded with a load of 500 grams and left to stand for a further period of 3 days under conditions of 35 °C and 80% relative humidity. The samples were then peeled apart, and the surfaces were examined.

The results obtained on the basis of the methods of evaluation described above are shown in Table 2.

35 A content of ammonium thiosulfate in permeated water in Run numbers 2, 3, 5, 6 and 7 were 0.02, 0.04, 0.23, 0.29 and 0.34 g/l, respectively.

40

45

50

55

Table 2

Run Number	Reverse Osmosis Membrane	Pressure for Solution feeding (kg/cm ²)	NaCl Removal Rate of the Membrane	Reticulation *	Fading of the Cyand Dye	Adhesion Proparties
1 (Comparison)	No treatment	-	-	+	34%	+
2 (")	DRA-98	15	98%	+	27%	-
3 (")	SU-700	12	92%	+	25%	-
4 (Invention)	DRA-89	7	89%	-	17%	-
5 (")	DRA-80	4	78%	-	13%	-
6 (")	SU-200	4	57%	-	14%	-
7 (")	DRA-40	5	38%	-	18%	+
8 (Comparison)	DRC-29	7	27%	+	26%	+

* + +: Large amount of reticulation +: Some reticulation -: No reticulation
 ** + +: Considerable adhesion +: Some adhesion -: No adhesion

Multi-Layer Color Printing Paper

5

The multi-layer color printing paper having the layer structure described below was prepared on a paper support which had been laminated on both sides with polyethylene. The coating solutions were prepared by mixing and dissolving the emulsions, various reagents and emulsified coupler dispersions. The methods of preparation are described in detail below.

10

Preparation of the Coupler Emulsion:

Ethyl acetate (27.2 cc) and 7.7 cc of solvent (Solv-1) were added to 19.1 grams of yellow coupler (ExY) and 4.4 grams of color image stabilizer (Cpd-1) and a solution was formed. This solution was emulsified and dispersed in 185 cc of a 10% aqueous gelatin solution which contained 8 cc of 10% sodium dodecylbenzenesulfonate.

The magenta, cyan and intermediate layer emulsions below were prepared in the same way. The compounds used in each emulsion are indicated below.

20

25

30

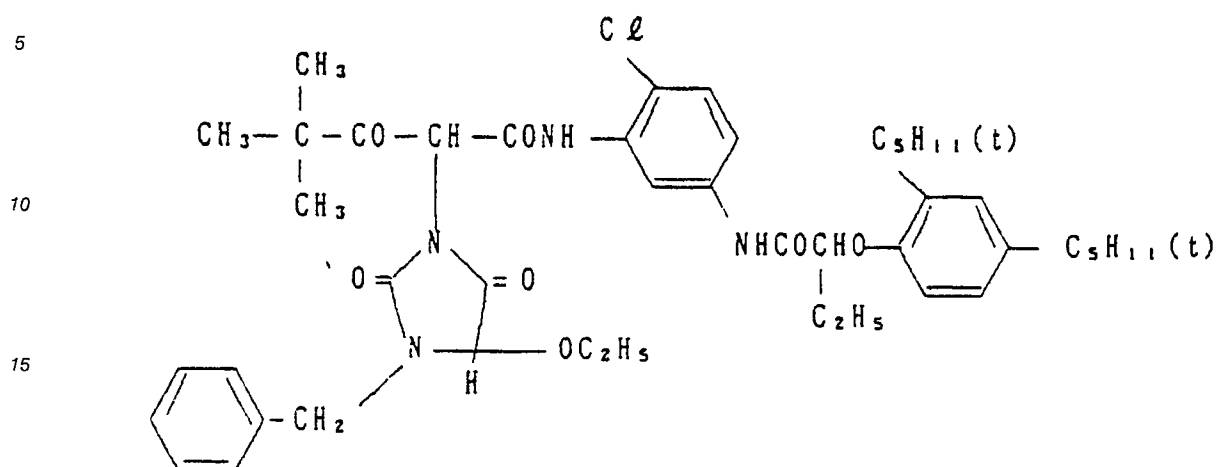
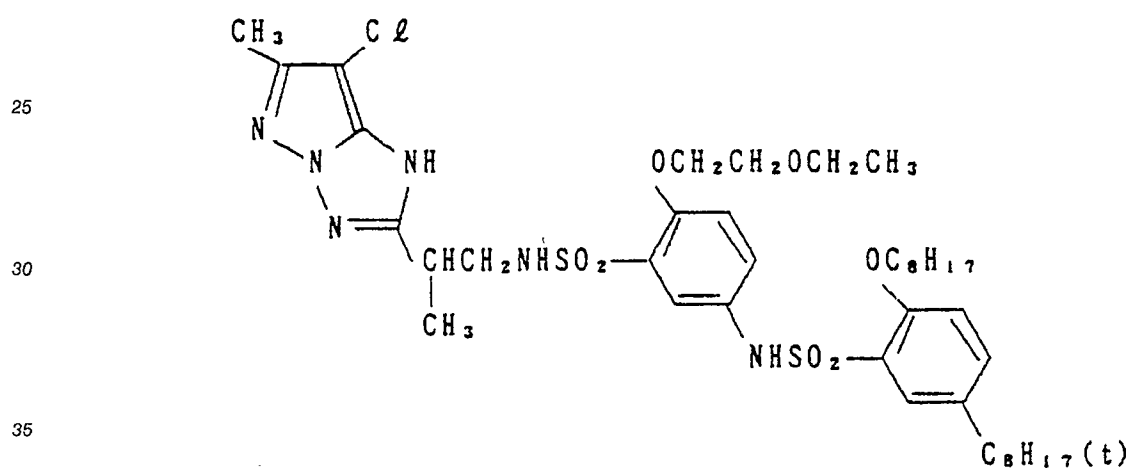
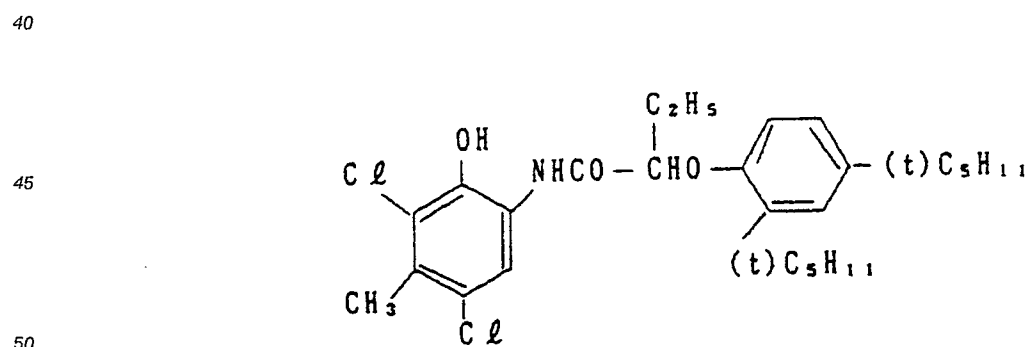
35

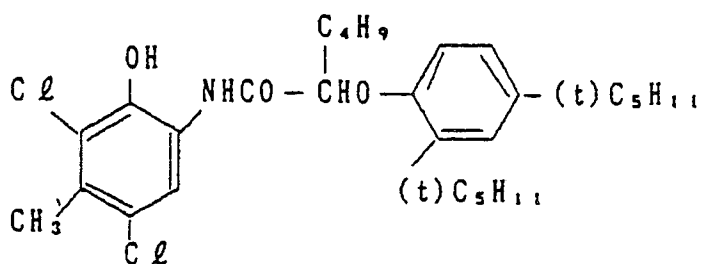
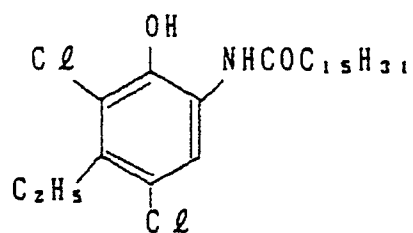
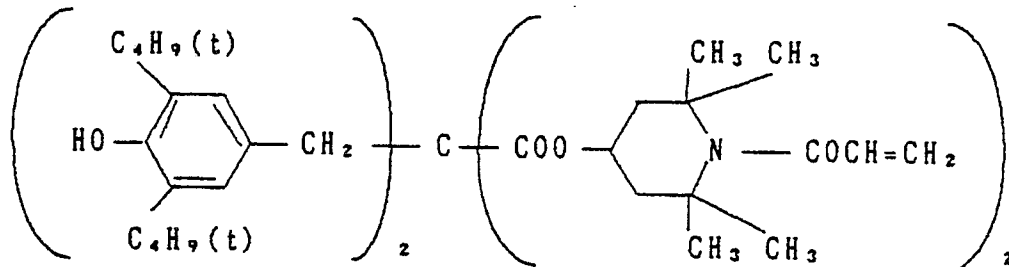
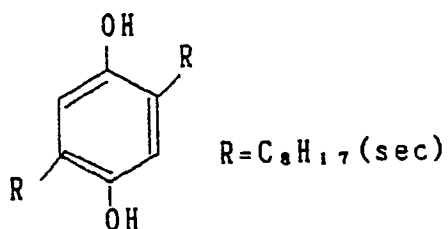
40

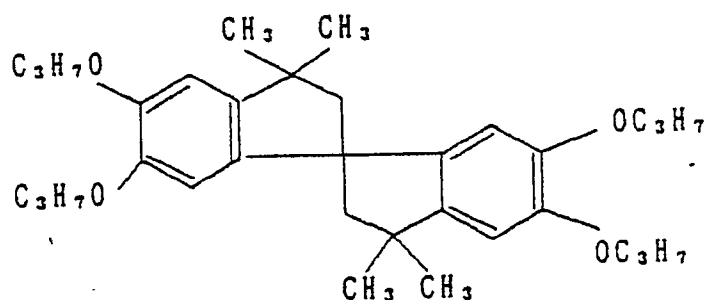
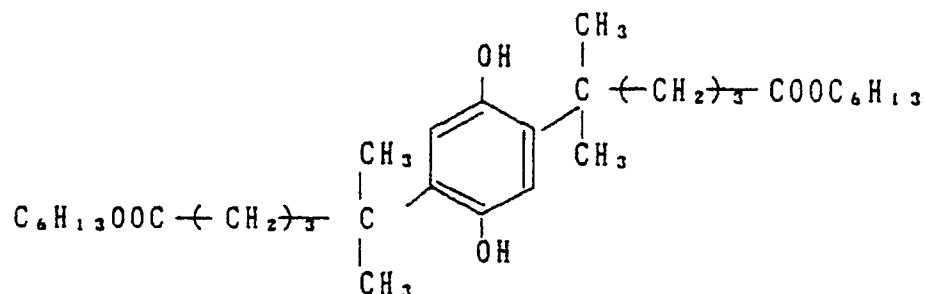
45

50

55

(ExY) Yellow Coupler(ExM-1) Magenta Coupler(ExC-1) Cyan Coupler

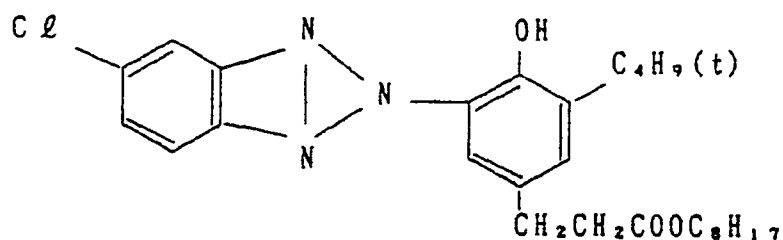
(ExC-2) Cyan Coupler(ExC-3) Cyan Coupler(Cpd-1) Color Image Stabilizer(Cpd-2) Anti-color Mixing Agent

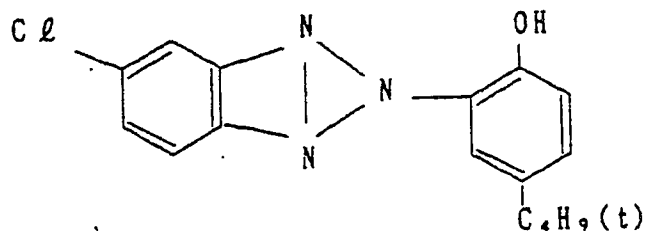
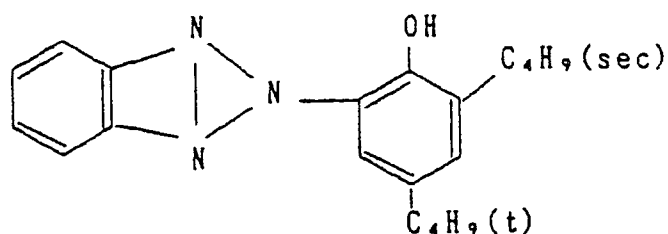
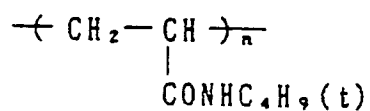
(Cpd-3) Color Image Stabilizer(Cpd-4) Color Image Stabilizer(Cpd-5) Anti-color Mixing Agent:

Same as Cpd-2 but $R = C_8H_{17}(t)$

(Cpd-6) Colored Image Stabilizer

A 5:8:9 (by weight) mixture of 6a:6b:6c

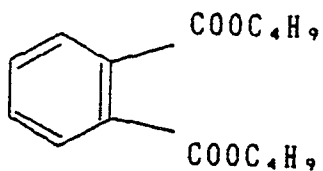
6a

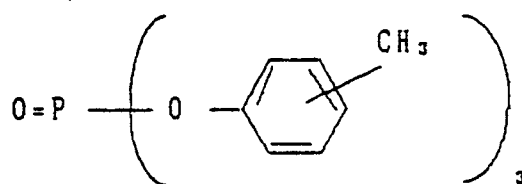
6b6c(Cpd-7) Polymer

Number Average Molecular Weight 80,000

(UV-1) Ultraviolet Absorber

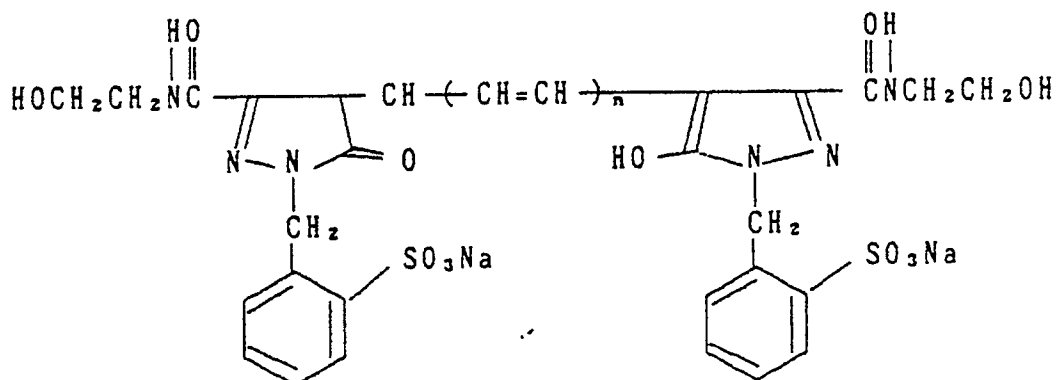
A 2:9:8 (by weight) mixture of 6a:6b:6c

(Solv-1) Solvent(Solv-2) Solvent $\text{O}=\text{P}-(\text{O}-\text{C}_8\text{H}_{17}(\text{iso}))_3$ (Solv-3) Solvent $\text{O}=\text{P}-(\text{O}-\text{C}_9\text{H}_{19}(\text{iso}))_3$ (Solv-4) Solvent



The dyes indicated below were added in an amount of 15 mg/m² for anti-irradiation purposes.

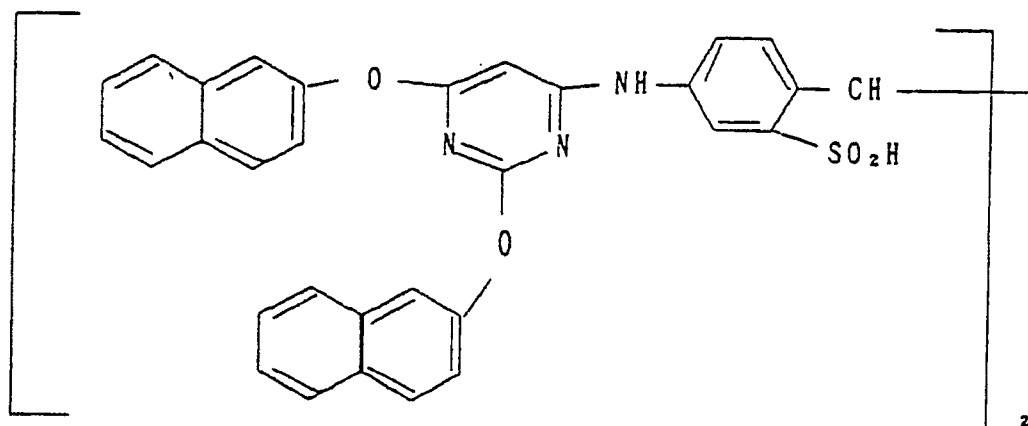
Red Layer: Dye-R



where $n = 2$

Green Layer: Same as Dye-R but with $n = 1$.

The compound indicated below was added at the rate of 2.6×10^{-3} mol per mol of silver halide to the red sensitive emulsion layer.



The emulsions used in this example are described below.

Blue Sensitive Emulsion:

A mono-disperse cubic silver chloride emulsion containing grains having an average size of 1.1 μm and a variation coefficient (the value s/d obtained by dividing the standard deviation by the average grain size) of 0.10 and containing K_2IrCl_6 and 1,3-dimethylimidazolin-2-thione was prepared in the same manner as disclosed in JP-A-2-100049, Example 1. Next, 26 cc of a 6% solution of the blue spectral sensitizing dye (S-1) was added to 1.0 kg of this emulsion, and a silver bromide fine grain emulsion having a grain size of 0.05 μm was added in the amount of 0.5 mol% with respect to the host silver chloride emulsion. After

ripening, sodium thiosulfate was added, and the mixture was chemically sensitized optimally. Then, 10^{-4} mol/mol*Ag of stabilizer (Stb-1) was added, and the emulsion was obtained.

5 Green Sensitive Emulsion :

A mono-disperse cubic silver chloride emulsion containing grains having an average grain size of 0.48 μm and a variation coefficient of 0.10 was prepared by preparing silver chloride grains which contained K_2IrCl_6 and 1,3-dimethylimidazolin-2-thione in the same manner as disclosed in JP-A-2-100049, Example 1,
10 and then adding 4×10^{-4} mol/mol*Ag of sensitizing dye (S-2) and KBr. After ripening, sodium thiosulfate was added, and chemical sensitization was carried out optimally. Then adding 5×10^{-4} mol/mol*Ag of stabilizer (Stb-1) was added to obtain the emulsion.

15 Red Sensitive Emulsion :

This emulsion was prepared in the same way as the green sensitive emulsion. However, the sensitizing dye (S-3) was used in an amount of 1.5×10^{-4} mol/mol*Ag instead of S-2.

The compounds used are indicated below.

20

25

30

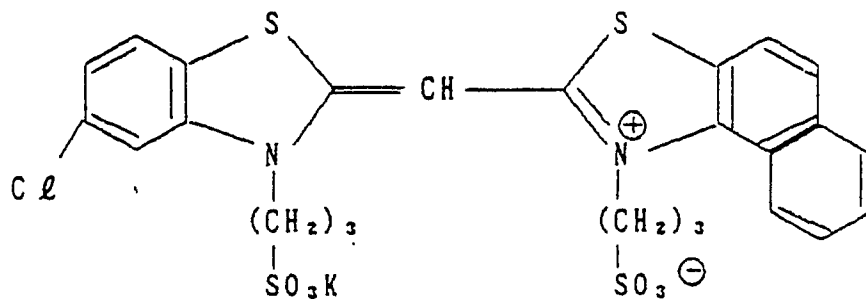
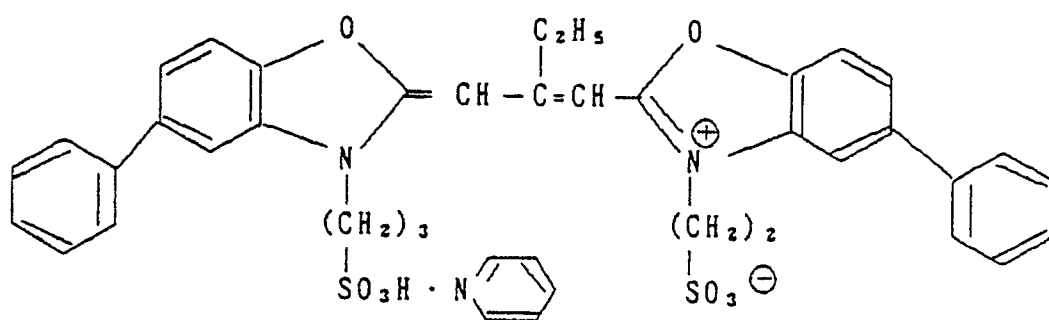
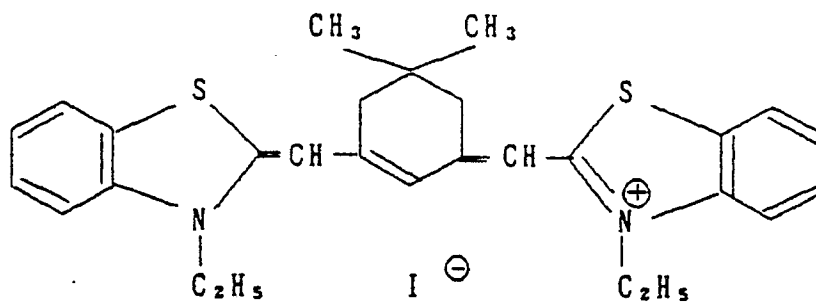
35

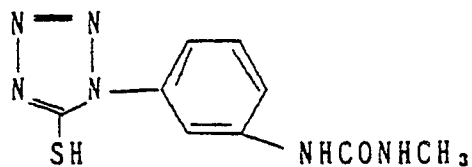
40

45

50

55

(S-1) Sensitizing Dye(S-2) Sensitizing Dye(S-3) Sensitizing Dye

(Stb-1) Stabilizer15 Layer Structure

The composition of each layer in the sample is indicated below. The numerical value indicates the coated weight (g/m²). The coated weights of silver halide emulsions are shown after calculation as silver.

20 Support

Polyethylene laminated paper. (White pigment (TiO₂) and blueing dye (ultramarine) were included in the polyethylene on the first layer side)

25

<u>First Layer</u> (Blue Sensitive Layer)	
Silver halide emulsion	0.30
Gelatin	1.86
Yellow coupler (ExY)	0.82
Color image stabilizer (Cpd-1)	0.19
Solvent (Solv-1)	0.35

30

35

<u>Second Layer</u> (Anti-color mixing layer)	
Gelatin	0.99
Anti-color mixing agent (Cpd-2)	0.08

40

45

<u>Third Layer</u> (Green Sensitive Layer)	
Silver halide emulsion	0.36
Gelatin	1.24
Magenta coupler (ExM-1)	0.31
Color image stabilizer (Cpd-3)	0.25
Color image stabilizer (Cpd-4)	0.12
Solvent (Solv-2)	0.42

50

55

Fourth Layer (Ultraviolet Absorbing Layer)	
Gelatin	1.58
Ultraviolet absorber (UV-1)	0.62
Anti-color mixing agent (Cpd-5)	0.05
Solvent (Solv-3)	0.24

Fifth Layer (Red Sensitive Layer)	
Silver halide emulsion	0.23
Gelatin	1.34
Cyan coupler (1:2:2 blend of ExC1:ExC2:ExC3)	0.34
Color image stabilizer (Cpd-6)	0.17
Polymer (Cpd-7)	0.40
Solvent (Solv-4)	0.23

Sixth Layer (Ultraviolet Absorbing Layer)	
Gelatin	0.53
Ultraviolet absorber (UV-1)	0.21
Solvent (Solv-3)	0.08

Seventh Layer (Protective Layer)	
Gelatin	1.33
Poly(vinyl alcohol) acrylic modified copolymer (17% Modification)	0.17
Solution paraffin	0.03

1-Oxy-3,5-dichloro-s-triazine, sodium salt, was used in each layer as a film hardening agent. The color printing paper prepared in the way described above was cut to a width of 82.5 mm.

EXAMPLE 2

The color negative film described below was cut to a width of 35 mm and then exposed in a camera and processed under the processing conditions described below on the basis of the processing operations indicated in Table 3 in the processing apparatus shown diagrammatically in Figure 2. Then, samples of film processed after 2 days of processing were evaluated in terms of (1) reticulation which occurred on storage and (2) fading of the cyan dye.

Processing Apparatus

In Figure 2, 21 is the development tank (D), 22 is the bleach tank (B), 23 and 24 are the first fixer tank (F₁) and the second fixer tank (F₂), respectively, 25, 26 and 27 are the first water washing tank (W₁), the second water washing tank (W₂) and the third water washing tank (W₃), respectively, and 28 is the

stabilizing tank. Fresh washing water 29 is supplied to the third water washing tank (W_3) 27 and washing water from this tank is fed to the second water tank 26 via the connecting pipe 30, and subsequently via the connecting pipe 31 to the first water washing tank (W_1) 25. The washing water 32 expelled therefrom as an overflow is supplied to the second fixer bath (F_2) 24 to provide a multi-stage counter-flow system. With the
5 fixer baths, the fixer from the second fixer bath (F_2) 24 is sent to the first fixer bath (F_1) 23.

Washing water was taken out via the flow pipe 33 from the second water washing tank (W_2) 26 and sent to the reverse osmosis membrane module (RO) 35 at a flow rate of 2 l/min by the pump (P) 11. The permeated water obtained from the reverse osmosis membrane module 35 was supplied at a flow rate of 100 to 180 ml/min via the connecting pipe 36 to the third water washing tank (W_3) 27, and the concentrate
10 was returned at a flow rate of 0.9 to 1.8 l/m via the connecting pipe 37 to the second water washing tank (W_2) 26.

The same reverse osmosis membranes as used in Example 1 were used in the reverse osmosis membrane module (RO) 35 under the pressure of 4.0 to 14 kg/cm².

The processing operations in this processing apparatus were as shown in Table 3.

15

20

25

30

35

40

45

50

55

Table 3 -Processing Operations

Process	Temperature	Processing Time	Tank Capacity	Replenishment Rate
Color Development	38°C	3 min. 15 sec.	10 liters	400 ml/m ²
Bleach	38°C	45 seconds	4 liters	130 ml/m ²
Fix (1)	38°C	45 seconds	4 liters	400 ml/m ²
Fix (2)	38°C	45 seconds	4 liters	
Water Wash (1)	38°C	15 seconds	2 liters	190 ml/m ²
Water Wash (2)	38°C	15 seconds	2 liters	
Water Wash (3)	38°C	15 seconds	2 liters	
Stabilizing	38°C	15 seconds	2 liters	
Drying	55°C			

<u>Color Developer</u>		<u>Mother Solution</u>	<u>Replenisher</u>
		<u>(g/l)</u>	<u>(g/l)</u>
Sodium sulfite		4.0	5.5
Potassium bromide		1.4	0.2
Potassium carbonate		39.0	40.5
Diethylenetriamine penta-acetic acid		1.0	1.2
1-Hydroxyethylidene-1,1-diphosphonic acid		3.3	3.7
Hydroxylamine		2.7	4.0
4-(N-Ethyl-N- β -Hydroxyethylamino)-2-methylaniline sulfate		4.5	6.5
Potassium hydroxide	to pH	10.05	10.18

<u>Bleach Bath</u>		<u>Mother Solution</u>	<u>Replenisher</u>
		<u>(g/l)</u>	<u>(g/l)</u>
1,3-Diaminopropane tetra-acetic acid, ferric ammonium salt, dihydrate		140	210
Acetic acid (90% aq. soln.)		35	50
Hydroxyacetic acid (70% aq. soln.)		97	140
Ammonium sulfate		40	60
Aqueous ammonia	to adjust to pH	3.6	2.5

Fixer Bath	Mother Solution	Replenisher
	(g/l)	(g/l)
Ammonium thiosulfate	200	350
Ammonium sulfite	20	35
Imidazole	22	40
Ethylenediamine tetra-acetic acid	10	18
Acetic acid	to adjust to pH	7.2
		7.4

Washing Water

Town water was passed through a mixed-bed column which had been packed with an H-type strongly acidic cation exchange resin ("Amberlite IR-120B" made by the Rohm and Haas Co.) and an OH-type anion exchange resin ("Amberlite IR-400", made by the same company) and water of the quality indicated below was obtained.

Calcium	0.3 mg/l
Magnesium	Less than 0.1 mg/l
pH	6.5
Electrical conductivity	5.0 μ S/cm

<u>Stabilizer Bath</u>		
(Mother Solution = Replenisher) Units: grams unless otherwise noted		
Formaldehyde (37% aq.soln.)		2.0 ml
Polyethylene-p-monononylphenyl ether (average degree of polymerization: 10)		0.3
Ethylenediamine tetra-acetic acid, disodium salt		0.05
Water (town water)	to make up to	1 liter
pH		5.0 - 8.0

Methods of Evaluation

Reticulation Occurring on Storage:

Reticulation was evaluated according to the method described in Example 1 above.

Fading of the Cyan Dye:

Samples which had been subjected to a 20 CMS wedge exposure at a color temperature of 4800K and processed were stored for 4 weeks under conditions of 70° C and 70% relative humidity, and the change in the maximum density region of the cyan dye was expressed as a percentage.

The results obtained on the basis of the method of evaluation described above are shown in Table 4.

Table 4

Run Number	Remarks	Reverse Osmosis Membrane	Amount of NaCl Removed by the Membrane	Reticulation *	Fading of the Cyan Dye
1	Comparison	No treatment	-	++	29%
2	Comparison	DRA-98	98%	++	18%
3	Comparison	SU-700	92%	++	18%
4	Invention	DRA-89	89%	+	15%
5	Invention	DRA-80	78%	-	12%
6	Invention	SU-200	57%	-	14%
7	Invention	DRA-40	38%	-	17%
8	Comparison	DRC-29	27%	+	26%

* ++: Large amount of reticulation +: Some reticulation -: No reticulation

Color Photosensitive Material

The multi-layer color photosensitive material was prepared by the lamination coating of layers having the compositions indicated below on a cellulose triacetate film support having a subbing layer.

Photosensitive Layer Composition

The numerical value corresponding to each component indicates the coated weight in units of g/m², and in the case of the silver halides, coated weights calculated as silver are shown. However, for the sensitizing dyes, the coated weights are indicated in units of mol per mol of silver halide in the same layer.

<u>First Layer (Anti-halation Layer)</u>		
Black colloidal silver	as silver	0.18
Gelatin		0.40

<u>Second Layer (Intermediate Layer)</u>	
2,5-Di-tert-pentadecylhydroquinone	0.18
EX-1 (Colored coupler)	0.07
EX-3 (")	0.02
EX-12 (Dye)	0.002
U-1 (Ultraviolet absorber)	0.06
U-2 (")	0.08
U-3 (")	0.10
HBS-1 (Dispersing oil)	0.10
HBS-2	0.02
Gelatin	1.04

Third Layer (First Red Sensitive Emulsion Layer)		
5	Mono-disperse silver iodobromide emulsion (silver iodide 6 mol%, average particle size 0.6 μm , variation coefficient of grain size 0.15)	as silver 0.55
	Sensitizing dye I	6.9×10^{-5}
	Sensitizing dye II	1.8×10^{-5}
	Sensitizing dye III	3.1×10^{-4}
10	Sensitizing dye IV	4.0×10^{-5}
	EX-2 (Cyan coupler)	0.350
	HBS-1 (Dispersing oil)	0.005
15	EX-10 (DIR coupler)	0.020
	Gelatin	1.20

Fourth Layer (Second Red Sensitive Emulsion Layer)		
25	Tabular silver iodobromide emulsion (silver iodide 10 mol%, average grain size 0.7 μm , average aspect ratio 5.5, average thickness 0.2 μm)	as silver 1.0
	Sensitizing dye I	5.1×10^{-5}
	Sensitizing dye II	1.4×10^{-5}
	Sensitizing dye III	2.3×10^{-4}
30	Sensitizing dye IV	3.0×10^{-5}
	EX-2 (Cyan coupler)	0.400
	EX-3 (Colored coupler)	0.050
	EX-10 (DIR coupler)	0.015
35	Gelatin	1.30

Fifth Layer (Third Red Sensitive Emulsion Layer)		
45	Silver iodobromide emulsion (silver iodide 16 mol%, average grain size 1.1 μm)	as silver 1.60
	Sensitizing dye IX	5.4×10^{-5}
	Sensitizing dye II	1.4×10^{-5}
	Sensitizing dye III	2.4×10^{-4}
	Sensitizing dye IV	3.1×10^{-5}
50	EX-3 (Colored coupler)	0.240
	EX-4 (Cyan coupler)	0.120
	HBS-1 (Dispersing oil)	0.22
	HBS-2 (")	1.10
55	Gelatin	1.63

5

Sixth Layer (Intermediate Layer)		
EX-5 (Anti-color mixing agent)	0.040	
HBS-1 (Dispersing oil)	0.020	
Gelatin	0.80	

10

Seventh Layer (First Green Sensitive Emulsion Layer)			
Tabular silver iodobromide emulsion (silver iodide 6 mol%, average grain size 0.6 μm , average aspect ratio 6.0, average thickness 0.15 μm)		as silver	0.40
Sensitizing dye V			3.0×10^{-5}
Sensitizing dye VI			1.0×10^{-4}
Sensitizing dye VII			3.8×10^{-4}
EX-6 (Magenta coupler)			0.260
EX-1 (Colored coupler)			0.021
EX-7 (")			0.030
EX-8 (DIR coupler)			0.025
HBS-1 (Dispersing oil)			0.100
HBS-4 (")			0.010
Gelatin			0.75

30

Eighth Layer (Second Green Sensitive Emulsion Layer)			
Mono-disperse silver iodobromide emulsion (silver iodide 9 mol%, average grain size 0.7 μm , variation coefficient of grain size 0.18)		as silver	0.80
Sensitizing dye V			2.1×10^{-5}
Sensitizing dye VI			7.0×10^{-5}
Sensitizing dye VII			2.6×10^{-4}
EX-6 (Magenta coupler)			0.180
EX-8 (DIR coupler)			0.010
EX-1 (Colored coupler)			0.008
EX-7 (")			0.012
HBS-1 (Dispersing oil)			0.160
HBS-4 (Dispersing oil)			0.008
Gelatin			1.10

55

Ninth Layer (Third Green Sensitive Emulsion Layer)		
Silver iodobromide emulsion (silver iodide 12 mol%, average grain size 1.0 μm)	as silver	1.2
Sensitizing dye V		3.5 x 10 ⁻⁵
Sensitizing dye VI		8.0 x 10 ⁻⁵
Sensitizing dye VII		3.0 x 10 ⁻⁴
EX-6 (Magenta coupler)		0.065
EX-11 (Colored coupler)		0.030
EX-1 (")		0.025
HBS-1 (Dispersing oil)		0.25
HBS-2 (")		0.10
Gelatin		1.74

20

Tenth Layer (Yellow Filter Layer)		
Yellow colloidal silver	as silver	0.05
EX-5 (Anti-color mixing agent)		0.08
HBS-3 (Dispersing oil)		0.03
Gelatin		0.95

30

Eleventh Layer (First Blue Sensitive Emulsion Layer)		
Tabular silver iodobromide emulsion (silver iodide 6 mol%, average grain size 0.6 μm, average aspect ratio 5.7, average thickness 0.15 μm)	as silver	0.24
Sensitizing dye VIII		3.5 x 10 ⁻⁴
EX-9 (Yellow coupler)		
EX-8 (DIR coupler)		
HBS-1 (Dispersing oil)		
Gelatin		1.28

45

50

55

5 10	Twelfth Layer (Second Blue Sensitive Emulsion Layer)		
	Mono-disperse silver iodobromide emulsion (silver iodide 10 mol%, average grain size 0.8 μm , variation coefficient of grain size 0.16)	as silver	0.45
	Sensitizing dye VIII		2.1×10^{-4}
	EX-9 (Yellow coupler)		0.20
	EX-10 (DIR coupler)		0.015
	HBS-1 (Dispersing oil)		0.03
	Gelatin		0.46

15 20 25	Thirteenth Layer (Third Blue Sensitive Emulsion Layer)		
	Silver iodobromide emulsion (silver iodide 14 mol%, average grain size 1.3 μm)	as silver	0.77
	Sensitizing dye VIII		2.2×10^{-4}
	EX-9 (Yellow coupler)		0.20
	HBS-1 (Dispersing oil)		0.07
	Gelatin		0.69

30 35	Fourteenth Layer (First Protective Layer)		
	Silver iodobromide emulsion (silver iodide 1 mol%, average grain size 0.07 μm)	as silver	0.5
	U-4 (Ultraviolet absorber)		0.11
	U-5 (")		0.17
	HBS-1 (Dispersing oil)		0.90
	Gelatin		1.00

40 45	Fifteenth Layer (Second Protective Layer)		
	Poly(methyl methacrylate) particles (average diameter about 1.5 μm)		0.54
	S-1 (Formaldehyde scavenger)		0.15
	S-2 (")		0.05
	Gelatin		0.72

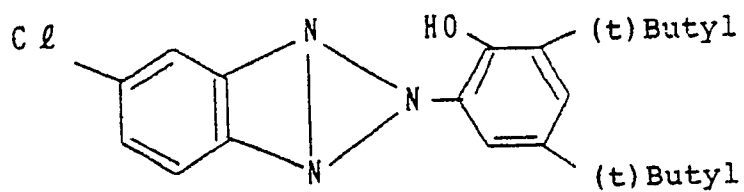
50 The gelatin hardening agent H-1 and a surfactant were added to each layer in addition to the components mentioned above.

55

U-1 (Ultraviolet absorber)

5

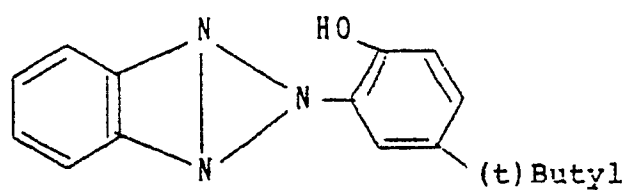
10



U-2 (Ultraviolet absorber)

15

20



25

30

35

40

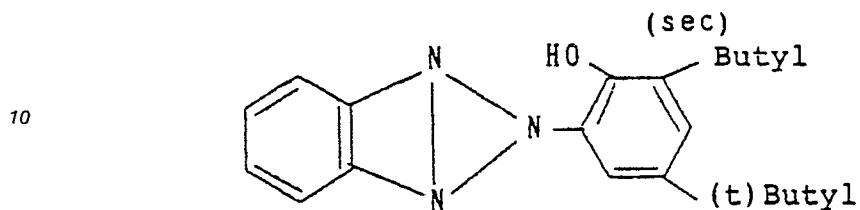
45

50

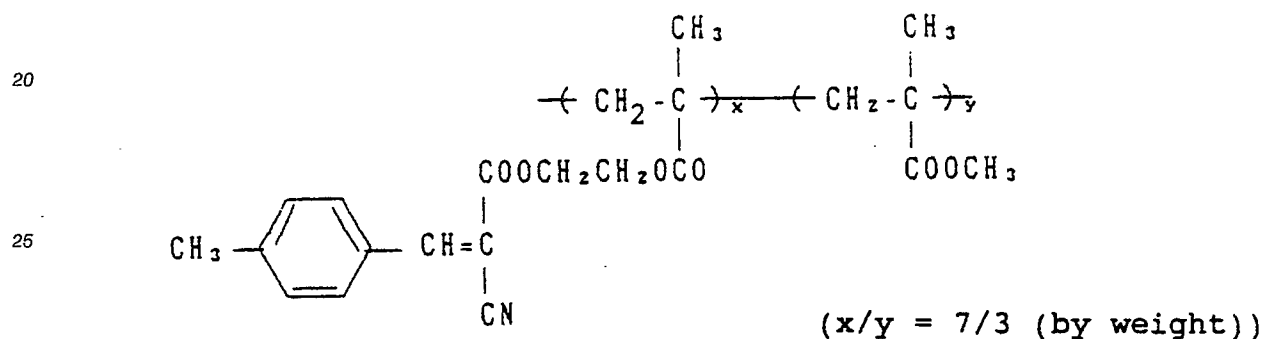
55

U-3 (Ultraviolet absorber)

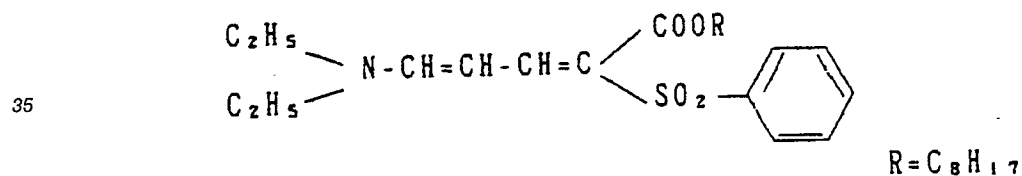
5

U-4 (Ultraviolet absorber)

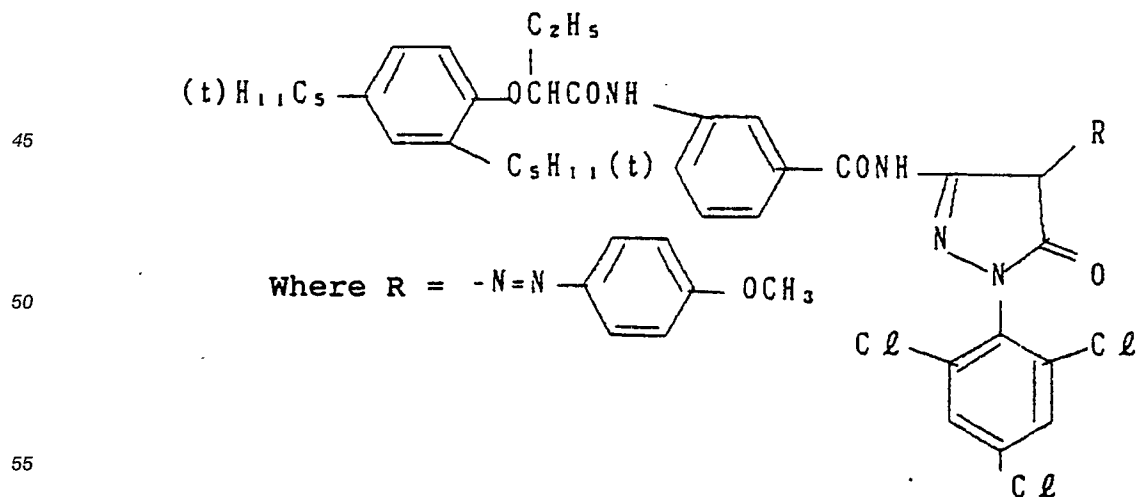
15

U-5 (Ultraviolet absorber)

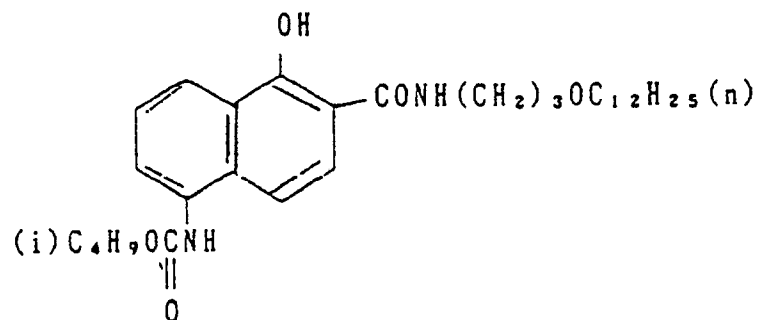
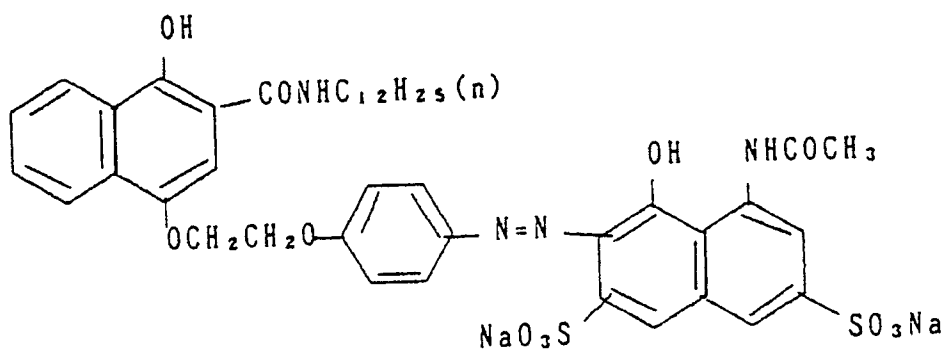
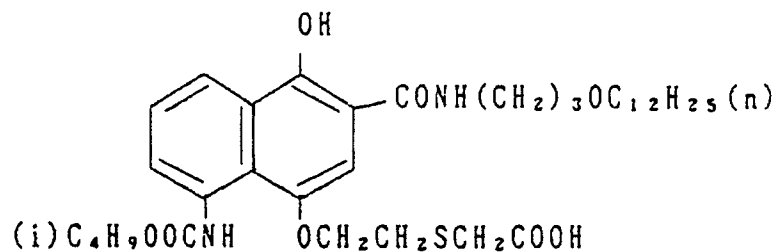
30

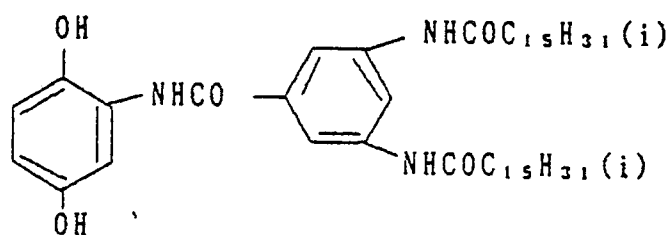
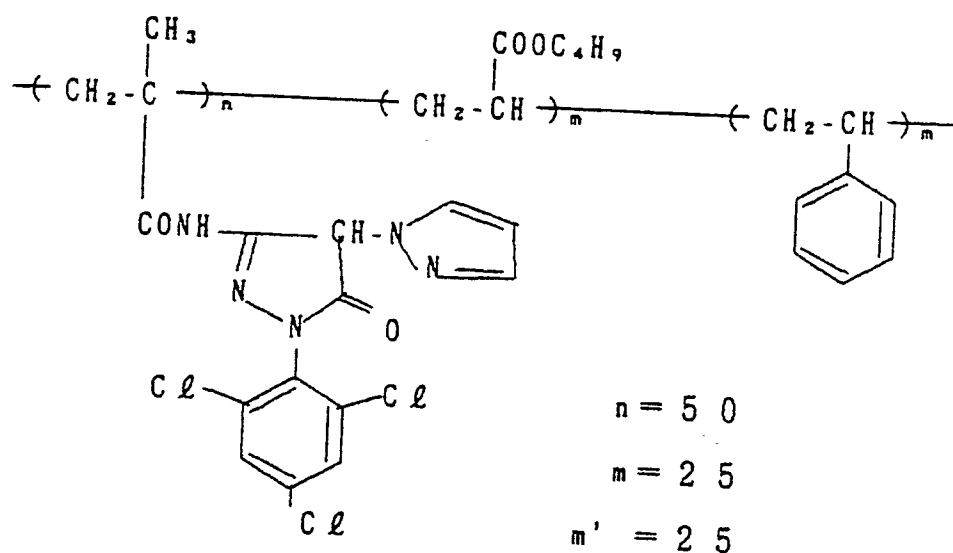
EX-1 (Colored coupler)

40



55

EX-2 (Cyan coupler)**EX-3** (Colored coupler)**EX-4** (Cyan coupler)

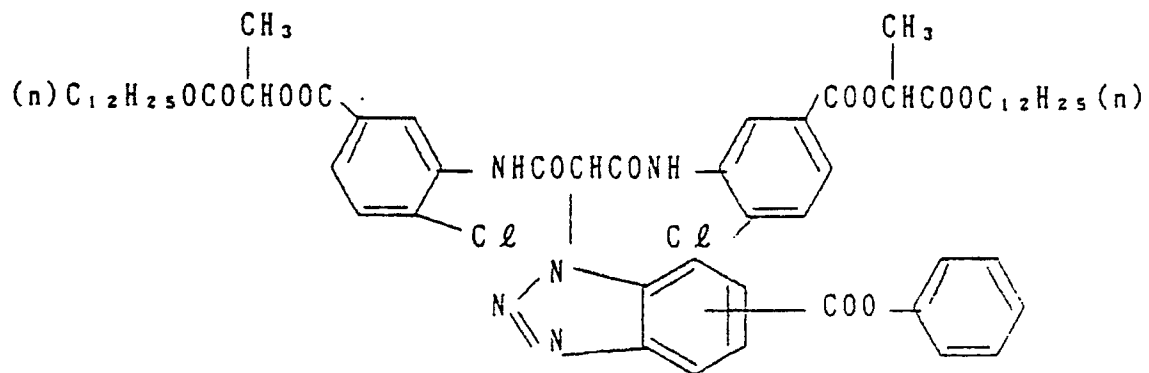
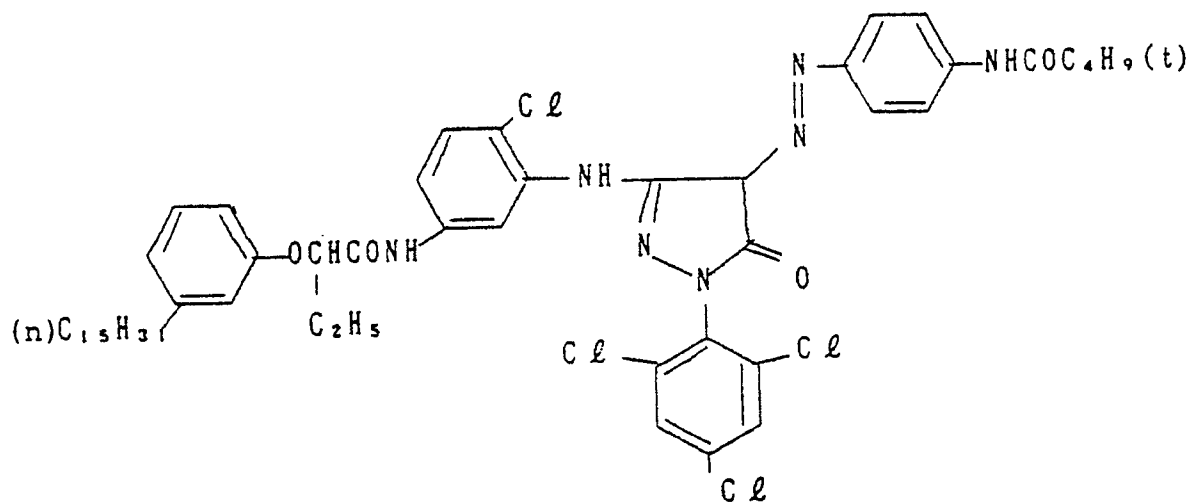
EX-5 (Anti-color mixing agent)EX-6 (Magenta coupler)

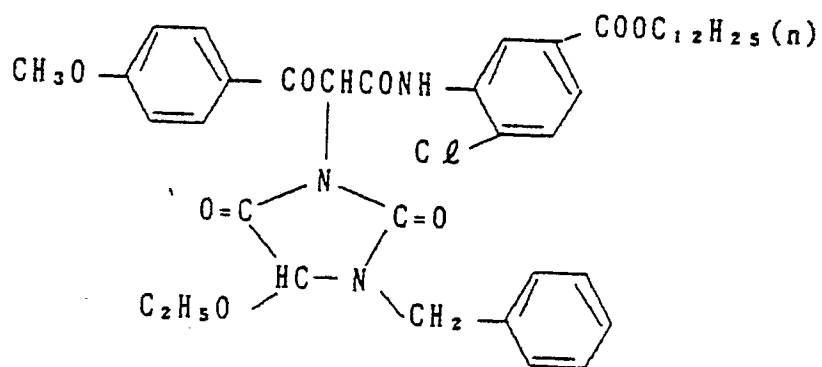
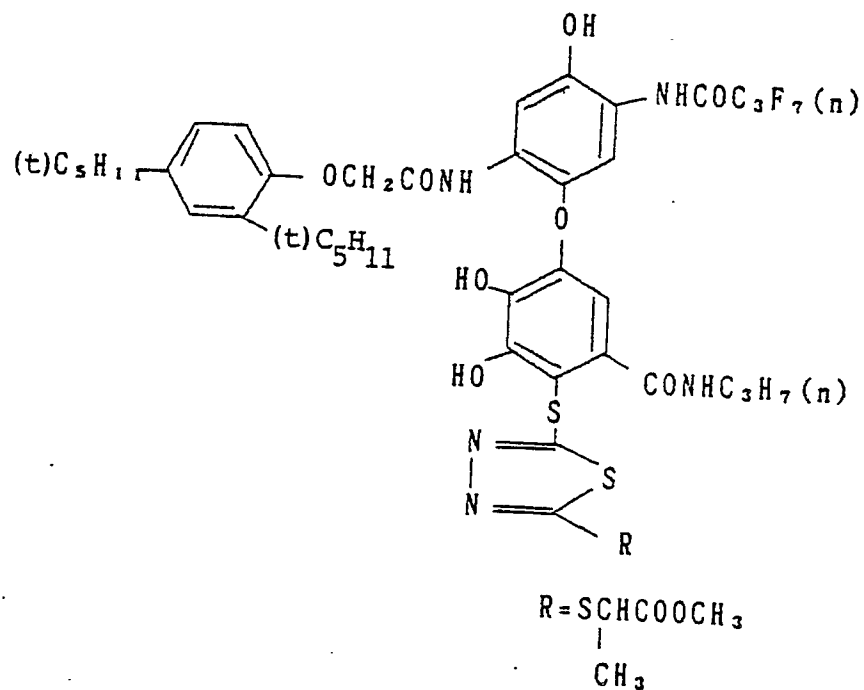
number average mol. wt. about 30,000

EX-7 (Colored coupler)



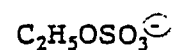
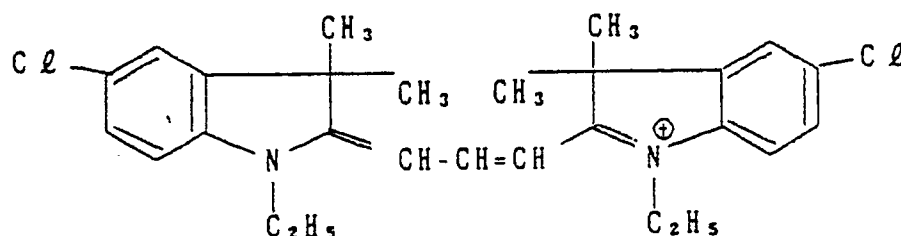
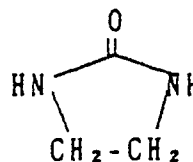
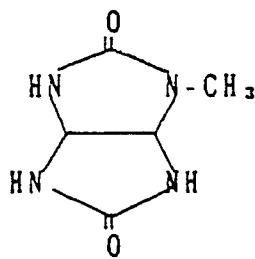
EX-8 (DIR coupler)



EX-9 (Yellow coupler)EX-10 (DIR coupler)

EX-11 (Colored coupler)

Same as EX-1 but R = H

EX-12 (Dye)S-1 (Formaldehyde scavenger)S-2 (Formaldehyde scavenger)HBS-1 (Dispersing oil)

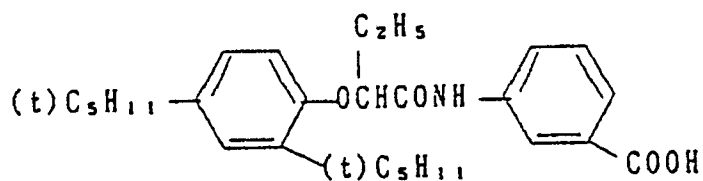
Tricresyl phosphate

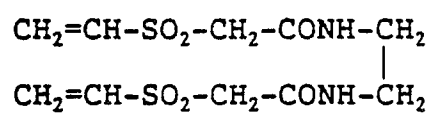
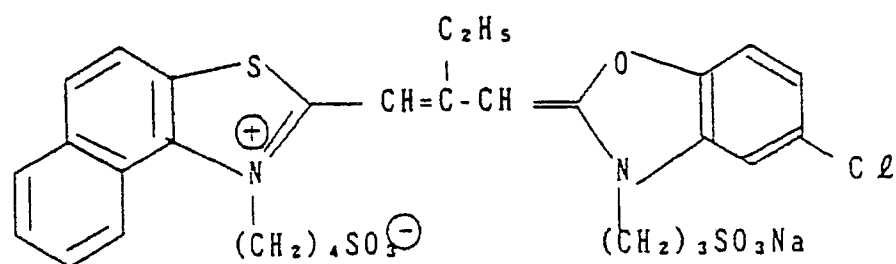
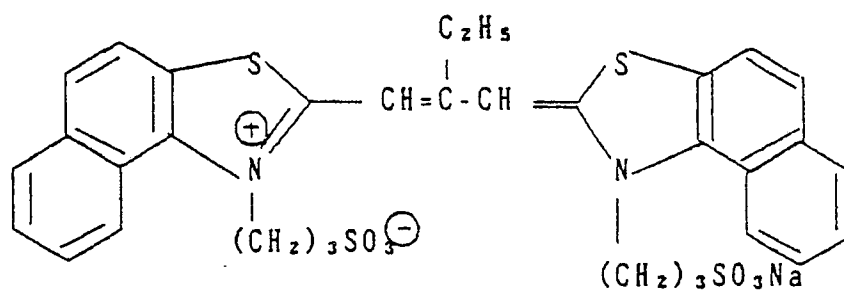
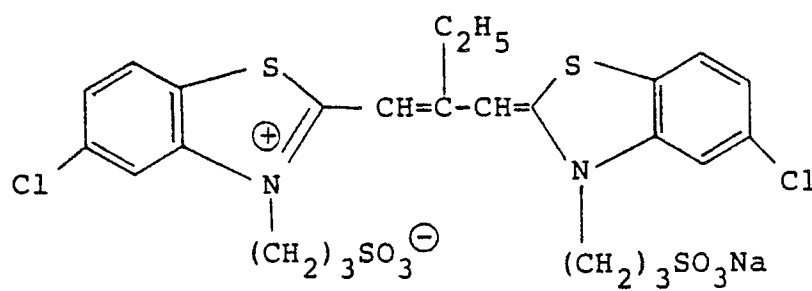
HBS-2 (Dispersing oil)

Dibutyl phthalate

HBS-3 (Dispersing oil)

Bis(2-ethylhexyl) phthalate

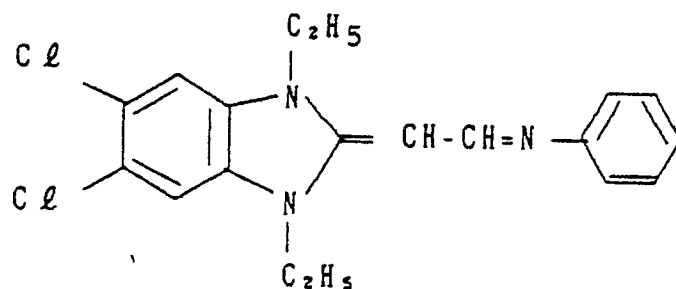
HBS-4 (Dispersing oil)

H-1Sensitizing DyesIIIIII

IV

5

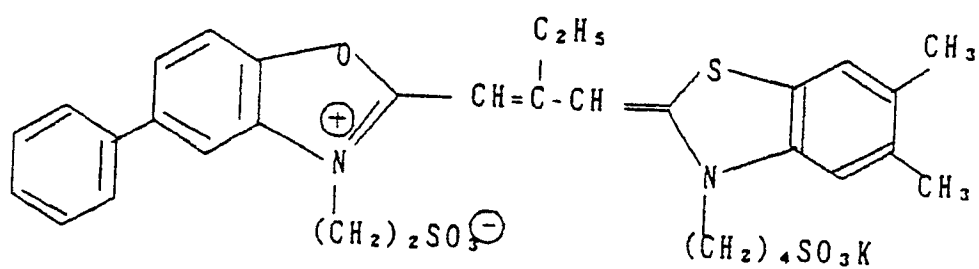
10

V

15

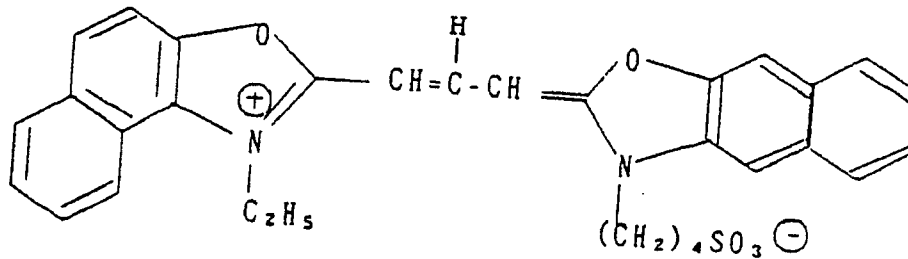
20

25

VI

30

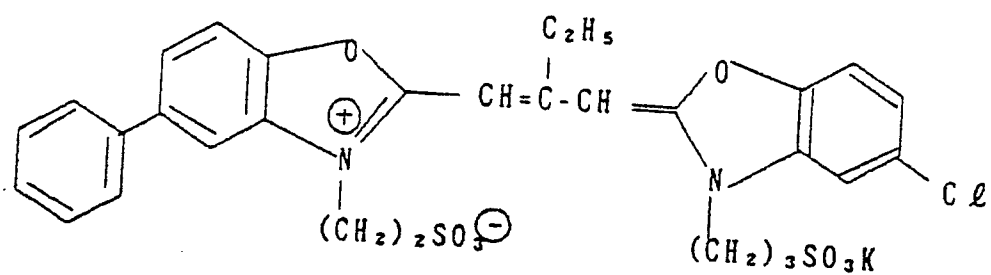
35

VII

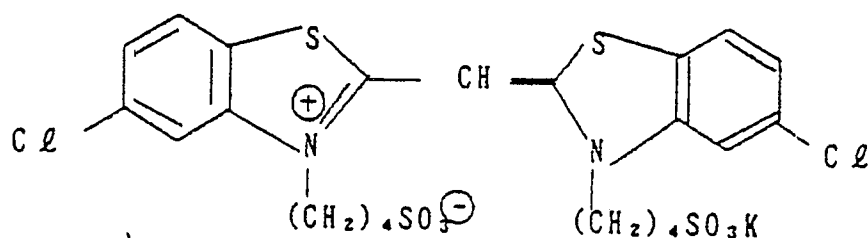
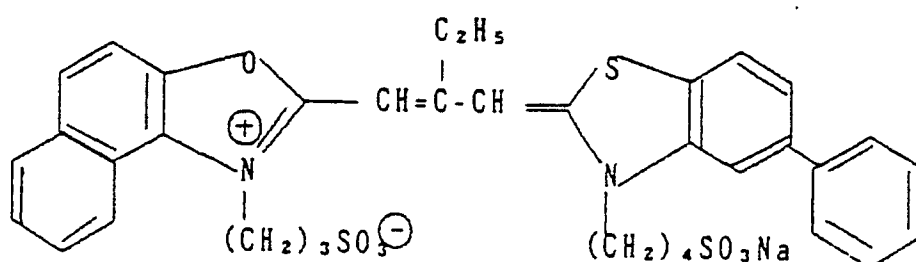
40

45

50



55

VIIIIX

Because the present invention uses a reverse osmosis membrane which removes NaCl in an amount of from 30 to 90%, there is no increase in the amino-polycarboxylic acid ferric complex salt concentration in the washing water or stabilizing solution and no increase in yellow staining even with a decrease in the amount of washing water and stabilizing solution used. Consequently, the amount of washing water or stabilizing solution can be significantly reduced.

Furthermore, no reticulation occurs, and there is no increased fading of the cyan dye. Moreover, the operating pressure in the reverse osmosis treatment is lower than that used conventionally, so the amount of work done is reduced and there is no increase in solution temperature due to heat generated by the pump. Additionally a high solution permeation rate can be maintained.

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

Claims

1. A method of processing silver halide photographic materials comprising processing, an imagewise-exposed halide photographic material in a bath which has a fixing ability and then processing the photographic material in at least one of a water washing bath and a stabilizing bath, wherein at least one of washing water and stabilizing solution, from at least one of the water washing bath and stabilizing bath, respectively, is subjected to a reverse osmosis treatment using a reverse osmosis membrane which removes NaCl in an amount of 30% to 90% when treating a 1000 ppm NaCl solution at 25° C under a feed pressure of 7 kg/cm².
2. A method of processing silver halide photographic materials as in claim 1, wherein at least one of the washing water and the stabilizing solution is replenished in at least one of the washing bath and the stabilizing bath at a rate of not more than 200 ml/m².
3. A method of processing silver halide photographic materials as in claim 1, wherein the reverse osmosis membrane is a synthetic composite membrane.
4. A method of processing silver halide photographic materials as in claim 1, wherein the reverse osmosis membrane that is used removes NaCl at a rate of 40% to 85% when treating a 1000 ppm NaCl solution at 25° C under a feed pressure of 7 kg/cm².
5. A method of processing silver halide photographic materials as in claim 4, wherein the reverse osmosis

membrane that is used removes NaCl at a rate of 50% to 80% when treating a 1000 ppm NaCl solution at 25° C under a feed pressure of 7 kg/cm².

6. A method of processing silver halide photographic materials as in claim 1, wherein the reverse osmosis membrane removes EDTA-Fe (III) in an amount of at least 90%.

5 7. A method of processing silver halide photographic materials as in claim 1, wherein four water washing baths are present, the washing water which is subjected to the reverse osmosis treatment is removed from the third water washing bath in the direction of material processing, and permeated water which has been subjected to the reverse osmosis membrane treatment is supplied to the fourth water washing bath in the direction of material processing.

10 8. A method of processing silver halide photographic materials as in claim 1, wherein four stabilizing baths are present, the stabilizing solution which is subjected to the reverse osmosis treatment is removed from the third stabilizing bath in the direction of material processing, and permeated water which has been subjected to the reverse osmosis membrane treatment is supplied to the fourth stabilizing bath in the direction of material processing.

15 9. A method of processing silver halide photographic materials as in claim 1, wherein the washing water and stabilizing solution are at a temperature of from 5° C to 40° C.

10. A method of processing silver halide photographic materials as in claim 9, wherein the temperature is from 10° C to 35° C.

20 11. A method of processing silver halide photographic materials as in claim 1, wherein the method of processing is a processing of silver halide color photographic material comprising a color development process and bleaching process.

25

30

35

40

45

50

55

FIGURE 1

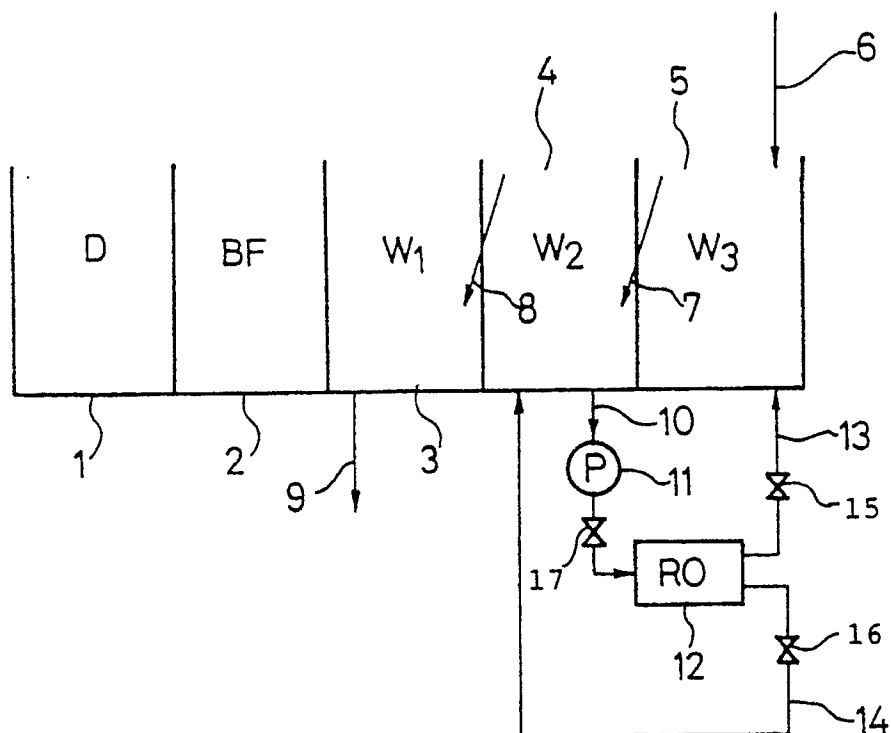
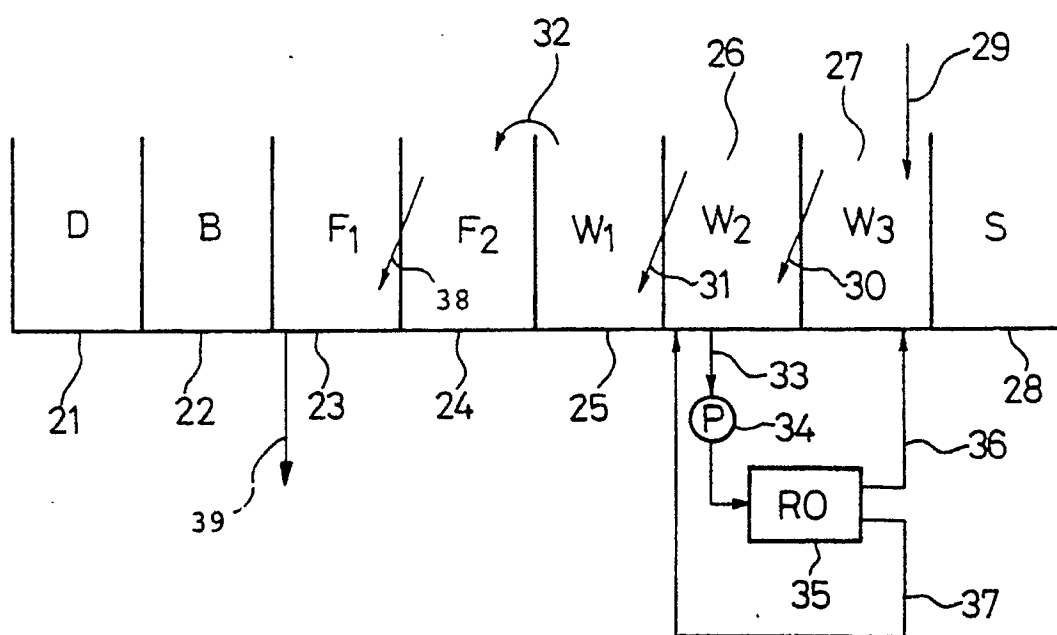


FIGURE 2





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 11 3278

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)
A, D	US-A-4451132 (S. KISHIMOTO) * the whole document *	1	G03C5/395 G03C7/44
A	US-A-4251624 (E. F. ENGLAND) * column 1, line 30 * * column 1, line 31 - column 34 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C G03D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11 OCTOBER 1990	Examiner BOLGER W.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			