⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 435 352 A1**

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: **90125786.5**

(51) Int. Cl.^{5}: **G03C 5/395**, G03C 7/42

㉒ Date of filing: **28.12.90**

㉚ Priority: **28.12.89 JP 338771/89**

㊸ Date of publication of application:
03.07.91 Bulletin 91/27

(84) Designated Contracting States:
BE DE FR GB IT NL

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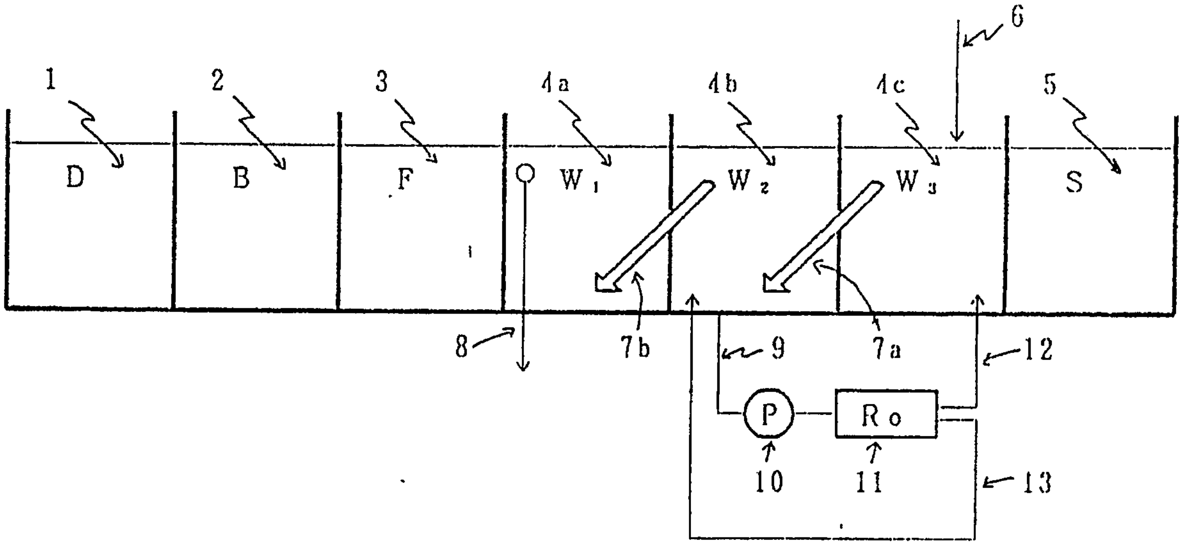
(54) A method of processing silver halide colour photographic photosensitive materials.

(57) A method of processing silver halide color photographic photosensitive materials for camera use which comprises processing the material in a bath which has a bleaching function and which contains, as a bleaching agent, an aminopolycarboxylic acid ferric complex salt followed by a multi-stage counter-flow water washing and/or stabilization processing wherein the molecular weight of the aminopolycarboxylic acid of the aminopolycarboxylic acid ferric complex salt is from 300 to 450 and the water washing water and/or stabilizer is treated by a reverse osmosis.

Fig. 1



EP 0 435 352 A1

A METHOD OF PROCESSING SILVER HALIDE COLOR PHOTOGRAPHIC PHOTOSENSITIVE MATERIALS

FIELD OF THE INVENTION

This invention concerns a method of processing silver halide color photographic photosensitive materials, mare particularly, it concerns an improved method of processing silver halide color photographic photosensitive materials for camera use, with which excellent images are obtained, even when the processing time after processing in a bath which has a bleaching function before reaching the drying process is shortened and the replenishment rates of the water washing water and/or stabilizer are reduced.

BACKGROUND OF THE INVENTION

Recently, new requirements have arisen in the processing of silver halide photographic photosensitive materials due to the increasing number of small in-store processing facilities known as mini-labs. One of these requirements is a shortened processing time and another is the reduction in the amount of waste liquid from the processing operation.

Shortening of the processing time is based on improving the service for producing prints while the customer waits without the need for the customer to make two visits to the store.

In connection with the shortening of processing times, research has been carried out on processing of silver halide color photographic photosensitive materials for color print purposes (referred to hereinafter as "color papers"). For example, the wet processing time prior to the drying operation has been shortened in practice to about 3 minutes for color papers in which silver chloride is used and which have been developed most recently.

In contrast, the processing of silver halide color photographic photosensitive materials for camera purposes (referred to hereinafter as "color negative films") takes a long time, a period of about 20 minutes, or of about 10 minutes in the case of especially rapid processing.

In particular, the coated silver weight and the developed silver weight are both high in high speed color negative films and a long period of time is required for the bleaching process. Furthermore, a ferric complex salt of ethylenediamine tetraacetic acid has been widely used in the past as a bleaching agent. However, in this case the bleaching rate is slow because of its weak oxidizing power and various bleaching accelerators have had to be used in combination. Even so, the amount of the processing time which has been shortened is still inadequate.

Most recently, bleach baths have been developed using bleaching agents which have a stronger bleaching power and a higher bleaching rate, such as ferric complex salts of 1,3-diaminopropane tetraacetic acid and cyclohexanediamine tetraacetic acid for example. However, a new problem has been discovered in that pronounced magenta staining arises on storage under conditions of high temperature and high humidity after rapid processing using these bleaches.

Next, a reduction in the amount of effluent in processing is required to prevent environmental pollution and to reduce the processing cost. Regenerating treatments for the processing effluent are difficult both in terms of equipment and in terms of cost with small scale installations such as mini-labs in particular and recovery and disposal of the processing waste liquids is essential. However, a large number of small scale processing facilities means that much effort is required for recovering the waste liquid and a reduction in the amount of waste liquid is especially desirable.

In connection with the reduction of the amount of waste liquid, although in comparison to the development of techniques in which replenishment rates are reduced to from 130 ml to 550 ml by improving the processing bath composition or the agitating system in the development process and the bleaching process, for example, when processing color negative films, large economies with respect to water usage have been achieved in the water washing and stabilization processes by reducing the rate of replenishment. Even with the introduction of multi-stage counter-flow water washing systems and multi-stage counter-flow stabilization systems, replenishment rates of some 800 ml per square meter of color negative film are still required and this is high when compared with the replenishment rate of some 350 ml/m^2 in the water washing and stabilizing processes used when color papers are processed.

The main reason why the rate of replenishment in the water washing and stabilization processes of color negative films cannot be reduced is the increased magenta staining which arises with storage under conditions of high temperature and high humidity after processing.

In particular, the increase in magenta staining is a serious problem when the replenishment rate of the water washing or stabilization processes is reduced where bleaching agents which have a high bleaching rate such as 1,3-diaminopropane tetraacetic acid ferric complex salt and cyclohexanediamine tetraacetic acid ferric complex salt are used and there are difficulties in practice.

SUMMARY OF THE INVENTION

Thus, there is a demand for the development of a technique which can both speed up the processing of camera silver halide color photographic photosensitive materials for use and reduce the amount of waste liquid which is formed during processing.

As a result of thorough research, the inventors have discovered that the above-described problems can be overcome by a method of processing silver halide color photographic photosensitive materials for camera use which includes processing in a bath which has a bleaching function containing, as a bleaching agent, an aminopolycarboxylic acid ferric complex salt followed by a multi-stage counter-flow water washing and/or stabilization process where the molecular weight of aminopolycarboxylic acid of the aminopolycarboxylic acid ferric complex salt is from 300 to 450 and the water washing water and/or stabilizer is subjected to treatment using reverse osmosis membrane.

In particular, the inventors discovered that the above-described problems could be resolved more effectively by including at least one compound selected from the group consisting of 1,3-diaminopropane tetraacetic acid ferric complex salt, 1,4-diaminobutane tetraacetic acid ferric complex salt, 1,5-diaminopentane tetraacetic acid ferric complex salt, trans-cyclohexanediamine tetraacetic acid ferric complex salt, glycol ether diamine tetraacetic acid ferric complex salt and diethylenetriamine pentaacetic acid ferric complex salt in the bath which has a bleaching function.

Moreover, it has been discovered that the above-described problems can be resolved more effectively by setting the processing time after processing in the bath which has a bleaching function until reaching the drying process to 6 minutes or less.

Furthermore, it has been discovered that the above-described problems can be overcome more effectively by reducing the rate of replenishment of the water washing water and/or stabilizer which is subjected to treatment with a reverse osmosis membrane to 800 ml or less per square meter of photosensitive material.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS

Figure 1 is a schematic drawing of the processing apparatus used in Example 1 in which a reverse osmosis membrane treatment apparatus is in the water washing process in accordance with the present invention.

Figure 2 is a schematic drawing of the processing apparatus used in Example 2 in which a reverse osmosis membrane treatment apparatus is in the stabilization process.

Figure 3 is a schematic drawing in which a reverse osmosis membrane treatment apparatus is in the water washing process when processing is carried out with a combination of two-tank counter-flow water washing and single tank stabilization.

Figure 4 is a schematic drawing in which a reverse osmosis membrane treatment apparatus is established in a four tank counter-flow stabilization process.

In the drawings, the reference numerals are as follows:

1: Color development tank (D)
2: Bleach Tank (B)
3: Fixer tank (F)
4, 4a - 4c. Water washing tanks (W, W_1, W_2, W_3)
5, 5a - 5d: Stabilizing tanks (S, S_1, S_2, S_3)
6: Fresh water replenishment pipe
7, 7a - 7c: Pipe for counter-flow purposes
8: Pipe for overflow
9: Pipe for liquid feed
10: Liquid feed pump
11: Pressure resistant apparatus which houses the reverse osmosis membrane
12: Permeating liquid pipe
13: Concentrated liquid pipe
14: Bleach-fix tank (BF)
15: Fresh stabilizer replenishment pipe

DETAILED DESCRIPTION OF THE INVENTION

In the method of processing silver halide color photographic photosensitive materials for camera use (referred to hereinafter as photosensitive materials) of the present invention, the imagewise exposed photosensitive material is color developed and then processed in a bath which has a bleaching function.

The bath which has a bleaching function which is used in the present invention is either a bleach bath or a bleach-fix bath which also has a fixing function.

In the present invention, the bath which has a bleaching function contains an aminopolycarboxylic acid ferric complex salt of which the molecular weight of the aminopolycarboxylic acid is at least 300 but not more than 450 as a bleaching agent, and this may take the form of a salt such as an ammonium, sodium or potassium salt for example.

The following are examples of aminopolycarboxylic acids of which the molecular weight is at least 300 but not more than 450.

1,3-Diaminopropane tetraacetic acid	306.3
1,4-Diaminobutane tetraacetic acid	320.3
1,5-Diaminopentane tetraacetic acid	334.3
Trans-cyclohexanediamine tetraacetic acid	346.4
Glycol ether diamine tetraacetic acid	380.4
Diethylenetriamine pentaacetic acid	393.4
1,2-Diaminopropane tetraacetic acid	306.3

The preferred bleaching agents in the present invention have a high bleaching rate when used in bleach baths and bleach-fix baths and those which have a molecular weight of at least 300 and not more than 400 are preferred in view of the excellent storage properties obtained when they are used in combination with a reverse osmosis membrane treatment, and the use of 1,3-diaminopropane tetraacetic acid, 1,4-diaminobutane tetraacetic acid, 1,5-diaminopentane tetraacetic acid, trans-cyclohexanediamine tetraacetic acid, glycol ether diamine tetraacetic acid and diethylenetriamine pentaacetic acid is preferred. When used in a bleach bath, 1,3-diaminopropane tetraacetic acid is especially preferred, while trans-cyclohexanediamine tetraacetic acid and diethylenetriamine pentaacetic acid are both especially preferred when a bleach-fix bath is being used.

The amount of these bleaching agents used in a bleach bath is from 0.1 mol/liter to 1 mol/liter. However, the use of from 0.2 to 0.5 mol/liter, and most preferably of from 0.25 to 0.4 mol/liter, provides a high bleaching rate and there is little concern about precipitation out of solution.

Furthermore, the amount of these bleaching agents used in a bleach-fix bath is from 0.05 mol/liter to 0.5 mol/liter, the use of from 0.1 to 0.4 mol/liter is preferred, and the use of from 0.15 to 0.3 mol/liter is especially desirable, since the bleaching rate and fixing rate are high and there is little concern about precipitation.

Other known aminopolycarboxylic acid ferric complex salts can be used in combination as bleaching agents in the present invention within the range where the effect of the present invention can be still be achieved. Examples of aminopolycarboxylic acids of these bleaching agents and their molecular weights are indicated below.

Ethylenediamine tetraacetic acid	292.3
Methylimino diacetic acid	147.1
Iminodiacetic acid	133.1
Nitrilo tri-acetic acid	191.1
Triethylenetetramine hexaacetic acid	494.5

In the present invention, the bath pH is preferably from 2 to 7 where the bath which has a bleaching function is a bleach bath. Moreover, a pH in the range from 3 to 6.5 is preferred, and a pH in the range from 3.2 to 5.5 is especially preferred, to increase the bleaching rate and minimizing bleach fogging.

Furthermore, the pH is preferably from 4 to 8 where the bath which has a bleaching function is a bleach-fix bath. A pH of from 4.5 to 7.0 is preferred, and a pH of from 5.0 to 6.5 is especially preferred, as a pH range in which the bleaching rate is high, the extent of bleach fogging is minimized and the fixer which is also present is stable.

The steps in the method of the present invention after processing in the bath which has a bleaching function until the drying process is reached are as described below.

(1) Bleach → Fix → Water Wash → Stabilization
(2) Bleach → Fix → Water Wash
(3) Bleach → Fix → Stabilization
(4) Bleach-fix → Water wash → Stabilization
(5) Bleach-fix → Water Wash
(6) Bleach-fix → Stabilization
(7) Bleach → Bleach-fix → Water Wash → Stabilization
(8) Bleach → Bleach-fix → Water Wash
(9) Bleach → Bleach-fix → Stabilization
(10) Bleach → Bleach-fix → Fix → Water Wash → Stabilization
(11) Bleach → Bleach-fix → Fix → Water Wash
(12) Bleach → Bleach-fix → Fix → Stabilization

If, in the above mentioned processes, the processing time after processing in the bath which has a bleaching function (bleach bath or bleach-fix bath) which contains a bleaching agent in accordance with the present invention until reaching the drying process is shortened to 6 minutes or less there is a pronounced increase in magenta staining as described earlier and this cannot be used in practice.

However, it is possible to prevent this increase in magenta staining effectively even when the above-described processing time is reduced to 6 minutes or less by installing reverse osmosis membrane treatment apparatus in the water washing and/or stabilizing process in accordance with the present invention and subjecting the water washing water and/or stabilizer to treatment with a reverse osmosis membrane.

The effect of preventing the occurrence of magenta staining of the present invention in this way is especially pronounced where the above-described treatment time is not more than 5 minutes, and it is even more pronounced when the above-described processing time is not more than 4 minutes. The effect is even more marked when the above-described processing time is not more than 3 minutes.

Here, the processing time after processing in the bath which has a bleaching function until reaching the drying process may comprise, for example, bleach → fix (1 minute 30 seconds) → water wash (50 seconds) → stabilization (20 seconds).

Furthermore, there is a pronounced increase in magenta staining of the type described earlier when the replenishment rate is reduced in the water washing and/or stabilization process. For example, when the replenishment rate is reduced to 800ml or less per square meter of photosensitive material there is a pronounced increase in magenta staining and this cannot be used in practice.

However, it is possible to effectively prevent this increase in magenta staining even when the replenishment rate is reduced to 800ml or less per square meter of photosensitive material by subjecting the water washing water and/or stabilizer to a reverse osmosis membrane treatment in accordance with the present invention. The effect of preventing the occurrence of magenta staining of the present invention is more pronounced where the replenishment rate is not more than 500 ml/m^2, and it is most pronounced when the replenishment rate is not more than 300 ml/m^2.

The reverse osmosis membrane which can be used in the water washing and/or stabilization process in the present invention may be a high pressure reverse osmosis membrane or a medium pressure reverse osmosis membrane, but a low pressure reverse osmosis membrane is preferred. More specifically, a reverse osmosis membrane providing a removal factor for NaCl in liquid which permeates the membrane on subjecting an aqueous solution containing 2000 ppm of NaCl to a reverse osmosis treatment under conditions of a temperature of 25° C, and a pressure of 5 kg/cm^2, is from 30% to 90% is preferred. When such a loose reverse osmosis membrane is used, the amount of liquid which permeates is high even at low pressure and it is also possible to prevent magenta staining effectively.

These reverse osmosis membranes may comprise a skin layer which controls the membrane performance such as the amount of water permeating the membrane and the removal factor, for example, and a support layer which supports the above described layer. The membrane may be an asymmetric membrane in which these are both made of the same material or a composite membrane in which they are both made of different materials. Cellulose acetate membranes and polyamide membranes are examples of asymmetric membranes, and composite membranes include synthetic composite membranes in which synthetic materials are used, such as those in which a skin layer is formed by coating polyetheyleneimine and tolylenediisocyanate onto a support layer comprising a polysulfone and those in which a skin layer is formed by the polymerization of furfuryl alcohol. Membrane details are disclosed in the supplement to Kagaku Kogyo, 29-7 entitled "The Development and Uses of Advanced Separation Techniques", pages 156 - 172, published by the Kagaku Kogyo Co. The use of these synthetic composite membranes is preferred in this present invention in view of their removal factors, the amounts of water permeated and their durability.

Specific examples of synthetic composite membranes include DRA-40, DBA-80 and DRA-89 made by Daicel Chemical Industries and SU-200, SU-210 and SU-220 made by Toray.

In the present invention, the feed pressure of the liquid to be treated which is supplied to the reverse osmosis membrane is preferably from 2 to 20 kg/cm^2, more preferably from 3 to 15 kg/cm^2, even more preferably from 3 to 10 kg/cm^2 and most desirably from 3 to 6 kg/cm^2.

In the present invention, reverse osmosis membrane treatment apparatus is used in the water washing process and/or stabilizing process, and the construction is described with reference to Figures 1 to 4.

Figure 1 is a schematic drawing of the processing apparatus used in Example 1 in which reverse osmosis membrane treatment apparatus in accordance with the present invention is placed in the water washing process.

In Figure 1, 1 is the color development tank (D), 2 is the bleach tank (B), 3 is the fixer tank (F), 4a, 4b and 4c are respectively the first water washing tank (W_1), the second water washing tank (W_2) and the third water washing tank (W_3), and 5 is the stabilizing tank (S). Fresh washing water for replenishment is supplied to the third water washing tank 4c by pipe 6 and washing water from this tank is sent to the second water washing tank 4b which is an earlier stage by means of the counter-flow pipe 7a and washing water is sent to the fist water washing tank 4a via the sequential counter-flow pipe work 7b. Then, the overflow from this tank is removed from the system as effluent via the overflow pipe 8 to form a three stage counter-flow water washing system. Furthermore, the single stabilization tank 5 is included after the third water washing tank 4c.

Washing water is removed from the second water washing tank 4b by means of liquid feed pipe 9 and sent by liquid feed pump 10 to the pressure resistant apparatus 11 which houses the reverse osmosis membrane. The liquid which permeates and passes through the reverse osmosis membrane is supplied to the third water washing tank 4c by the permeating liquid pipe 12 and the concentrated liquid which does not pass through the reverse osmosis membrane is returned to the second water washing tank 4b by concentrated liquid pipe 13.

Figure 2 is a schematic drawing of the processing apparatus used in Example 2 in which a reverse osmosis membrane treatment apparatus in accordance with the present invention is placed in the stabilization process.

In Figure 2, 1 is the color development tank (D), 14 is the bleach-fix tank (BF), and 5a, 5b and 5c are respectively the first stabilization tank (S_1), the second stabilization tank (S_2) and the third stabilization tank (S_3). Fresh stabilizer for replenishment purposes is supplied to the third stabilization tank 5c by means of pipe 15, and stabilizer from the same tank is sent to the second stabilization tank 5b which is the previous stage by means of the counter-flow pipe 7a, and to the first stabilization tank 5a via the sequential counter-flow pipe 7b. Then, the overflow from here is removed from the system as effluent via overflow pipe 8 to provide a three stage counter-flow stabilization system.

Stabilizer is removed from the second stabilization tank 5b by means of liquid feed pipe 9 and sent to the pressure resistant apparatus 11 which houses the reverse osmosis membrane by means of liquid feed pump 10. The permeating liquid which permeates and passes through the reverse osmosis membrane is supplied to the third stabilization tank 5c by permeated liquid pipe 12 and the concentrated liquid which has not passed through the reverse osmosis membrane is returned to the second stabilization tank 5b by concentrated liquid pump 13.

Figure 3 is a schematic diagram of an apparatus in which reverse osmosis membrane treatment apparatus in accordance with the present invention is used in the water washing process in a processing system which includes a two stage counter-flow water washing process and a single tank stabilization process. Thus, water washing water is removed from the first water washing tank 4a by liquid feed pipe 9 and fed to the pressure resistant apparatus 11 which houses the reverse osmosis membrane by means of liquid feed pump 10. The liquid which permeates and passes through the reverse osmosis membrane is supplied to the second water washing tank 4b by means of permeated liquid pipe 12 and the concentrated liquid which has not passed through the reverse osmosis membrane is returned to the first water washing tank 4a by concentrated liquid pipe 13.

Figure 4 is a schematic drawing of a reverse osmosis membrane treatment apparatus in accordance with the present invention in a four stage counter-flow stabilization process. Thus, stabilizer is removed from the third stabilization tank 5c by means of liquid feed pipe 9 and sent to pressure resistant apparatus 11 which houses the reverse osmosis membrane by liquid feed pump 10. The liquid which permeates and passes through the reverse osmosis membrane is supplied to the fourth stabilization tank 5d by means of permeated liquid pipe 12 and the concentrated liquid which has not passed through the reverse osmosis membrane is returned to third stabilization tank 5c by the concentrated liquid pipe 13.

The color development tank, the bleach tank and the bleach-fix tank are not shown in Figures 3 and 4 but, needless to say, they are established in the same way as indicated in Figures 1 and 2 described above.

In the present invention, the color photographic photosensitive material can be developed and processed using conventional methods as disclosed in Research Disclosure (RD) No. 17643, pages 28 - 29 and in ibid, No. 18716 in the left to right hand columns of page 615.

The color developers used in the development processing of the photosensitive material are preferably aqueous alkaline solutions which contain a primary aromatic amine based color developing agent as the principal component. Aminophenol based compounds are also useful as color developing agents, but the use of p-phenylenediamine based compounds is preferred. Typical examples include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-β-methoxyethylaniline, and the sulfate, hydrochloride and p-toluenesulfonate salts of these compounds. Of these compounds, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline sulfate is especially preferred. Two or more of these compounds can be used conjointly, depending on the intended purpose.

The color developer generally contains pH buffers such as alkali metal carbonates, borates or phosphates, and development inhibitors or anti-foggants such as chlorides, bromides, iodides, benzimidazoles, benzothiazoles or mercapto compounds. The color developer may also contain, as required, various preservatives such as hydroxylamine, diethylhydroxylamine, sulfite, hydrazines such as N,N-biscarboxymethylhydrazine, phenylsemicarbazides, triethanolamine and catecholsulfonic acids, organic solvents such as ethylene glycol and diethylene glycol, development accelerators such as polyethylene glycol, quaternary ammonium salts and amines, dye forming couplers, competitive couplers, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, thickeners and various chelating agents exemplified by aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids and phosphonocarboxylic acids. Typical examples of these compounds include ethylenediamine tetraacetic acid, nitrilo triacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N,N-tetramethylenephosphonic acid, ethylenediamine-di(o-hydroxyphenylacetic acid) and the salts thereof.

Furthermore, color development is carried out after a normal black and white development in the case of reversal processing. Known black and white developing agents including dihydroxybenzenes such as hydroquinone, 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, and aminophenols such as p-aminophenol, for example, can be used individually, or in combination, in the black and white developer.

The pH of these color developers and black and white developers is generally from 9 to 12. Furthermore, the replenishment rate for these developers depends on the color photographic photosensitive material which is being processed but, in general, it is 3 liters or less per square meter of photosensitive material and it can be 500 ml or less by reducing the bromide ion concentration in the replenisher. Where the replenishment rate is low it is preferred that evaporation and aerial oxidation of the liquid should be prevented by minimizing the area of contact with the air in the processing tank.

The contact area between the air and the photographic processing bath in a processing tank can be represented by the open factor which is defined below.

$$\text{Open Factor} = \frac{\text{Processing bath and Air Contact Area (cm}^2\text{)}}{\text{Processing Bath Volume (cm}^3\text{)}}$$

The open factor is preferably less than 0.1, and more preferably from 0.001 to 0.05.

In addition to the use of a shielding material such as a floating lid, for example, on the surface of the photographic processing bath in the processing tank, the method involving the use of a movable lid as disclosed in JP-A-1-82033 and the method involving slit development processing disclosed in JP-A-63-216050 can be used to reduce the open factor.

Reduction in the open factor is preferably applied not only to color development and black-and-white development processes but also to all subsequent processes, such as the bleaching, bleach-fixing, fixing, water washing and stabilizing processes.

Furthermore, the replenishment rate can be reduced by using by suppressing the accumulation of bromide ion in the development bath.

The color development processing time is between 2 and 5 minutes, but shorter processing times can be achieved by increasing the pH and the temperature or by using a higher concentration of the color developing agent.

The photosensitive material is generally processed in a bath which has a bleaching function after color development.

As described above, the bleaching process may be carried out at the same time as a fixing process (in a bleach-fix process) or it may be carried out as a separate process.

Moreover, a bleach-fix process can be carried out after a bleaching process in order to speed up processing. Moreover, the processing can be carried out in two connected bleach-fix baths, a fixing process can be carried out before a bleach-fixing process or a bleaching process can be carried out after a bleach-fix process, as required.

The above-described bleaching agents in accordance with the present invention are used for the bleaching agent.

Bleaching accelerators can be used, as required, in the bleach baths, bleach-fix baths or bleach or bleach-fix pre-baths. Specific examples of useful bleach accelerators are the compounds which have a mercapto group or a disulfide group disclosed, for example, in U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426, and Research Disclosure No. 17129 (June 1978); the thiazolidine derivatives disclosed in JP-A-50-140129; the thiourea derivatives disclosed in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735 and U.S. Patent 3,706,561, the iodides disclosed in West German Patent 1,127,715 and JP-A-58-16235; the polyoxyethylene compounds disclosed in West German Patents 966,410 and 2,748,430; the polyamine compounds disclosed in JP-B-45-8836; the other compounds disclosed in JP-A-49-42434, JP-A-49-40943, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506 and JP-A-58-163940; and the bromide ion. Of these compounds, those which have a mercapto group or a disulfide group are preferred in view of their large accelerating effect, and the compounds disclosed in U.S. Patent 3,893,858, West German Patent 1,290,812 and JP-A-53-95630 are especially preferred. Moreover, the compounds disclosed in U.S. Patent 4,552,834 are also preferred. These bleaching accelerators may also be added to the sensitive material. These bleaching accelerators are especially effective when bleach-fixing color photosensitive materials for camera use.

Re-halogenating agents, such as bromides (for example potassium bromide, sodium bromide, ammonium bromide) or chlorides (for example potassium chloride, sodium chloride, ammonium chloride) can also be present in the bleach or bleach-fixer, and the use of ammonium bromide is preferred. The re-halogenating agent concentration is from 0.1 to 5 mol/liter, and preferably from 0.5 to 3 mol/liter.

Moreover, the use of ammonium nitrate as a metal corrosion inhibitor is also preferred.

In addition to the compounds described above, preferably the bleach or bleach fixer can contain organic acids to prevent the occurrence of bleach staining. The most preferred organic acids are compounds which have an acid dissociation constant (pKa) of from 2 to 5, and preferred examples include acetic acid, hydroxyacetic acid, lactic acid, propionic acid, tartaric acid, and citric acid. Acetic acid and hydroxyacetic acid are especially preferred. The amount of these organic acids is from 0.1 to 3 mol/liters, preferably from 0.5 to 2 mol/liter, and most preferably from 0.8 to 1.5 mol/liter.

Thiosulfate, thiocyanate, thioether based compounds, thioureas and large amounts of iodide can be used, for example, as the fixing agent which is used in the fixer or bleach-fixer, but thiosulfate is generally used. Ammonium thiosulfate in particular can be used in the widest range of applications. Furthermore, the combined use of thiosulfate and thiocyanate, thioether compounds, thiourea etc. is also preferred. Sulfite, bisulfite, carbonyl/bisulfite addition compounds or the sulfinic acid compounds disclosed in European Patent 294,769A are preferred as preservatives for fixers and bleach-fixers.

Moreover, the addition of various aminopolycarboxylic acids and organophosphonic acids to the fixers and bleach-fixers is preferred for stabilizing these baths.

The total de-silvering process time is preferably as short as possible as long as insufficient de-silvering does not occur. The preferred de-silvering time is from 1 to 3 minutes, and most preferably the de-silvering time is from 1 to 2 minutes. Furthermore, the processing temperature is from 25° C to 50° C, and preferably from 35° C to 45° C. The desilvering rate is improved and staining after processing is effectively prevented within the preferred temperature range.

The de-silvering baths are preferably agitated as strongly as possible during the de-silvering process.

Specific examples of methods of achieving strong agitation include methods in which a processing liquid is jetted against the emulsion surface of the photosensitive material as disclosed in JP-A-62-183460 and JP-A-62-183461, methods in which the agitation effect is increased using a rotary device as disclosed in JP-A-62-183461, methods in which the photosensitive material is moved with a wiper blade which is established in the bath in contact with the emulsion surface and the agitation effect is increased by the generation of turbulence at the emulsion surface, and methods in which the circulating flow rate of the processing bath as a whole is increased. These means of increasing agitation are effective for bleaches, bleach-fixers and fixers. It is thought that increased agitation increases the rate of supply of bleaching agent and fixing agent to the emulsion film and consequently increases the de-silvering rate. Furthermore, the above-described means of increasing agitation are more effective where a bleaching accelerator is used, and they sometimes provide a marked increase in the accelerating effect and eliminate the fixer inhibiting action of the bleaching accelerator.

Automatic processors used for processing photosensitive materials preferably have photosensitive material transporting devices as disclosed in JP-A-60-191257, JP-A-60-191258 or JP-A-60-191259. With such a transporting device, such as that disclosed in JP-A-60-191257, the carry over of processing bath from one bath to the next is greatly reduced and this is very effective for preventing deterioration in processing bath performance. These effects are especially useful for shortening the processing time in each process and for reducing the replenishment rate of each processing bath.

The silver halide color photographic photosensitive materials of this invention are generally subjected to a water washing process and/or stabilizing process after the desilvering process. The amount of wash water used in the washing process can be fixed within a wide range, depending on the application and the nature (depending on materials such as couplers which are used, for example) of the photosensitive material, the wash water temperature, the number of water washing tanks (the number of water washing stages) and the replenishment system, i.e. whether a counter-flow or a sequential flow system is used, and various other conditions. The relationship between the amount of water used and the number of washing tanks in a multi-stage counter-flow system can be obtained using the method outlined on pages 248 - 253 of the Journal of the Society of Motion Picture and Television Engineers, Volume 64 (May 1955).

The amount of wash water used can be greatly reduced by using the multi-stage counter-flow system described in the literature above, but bacteria proliferate due to the increased residence time of the water in the tanks and problems arise with suspended matter which is produced and attaches to the photosensitive material. The method in which the calcium ion and magnesium ion concentrations are reduced, as disclosed in JP-A-62-288838, is very effective as a means of overcoming this problem in the method of processing color photosensitive materials of the present invention. Furthermore, the isothiazolone compounds and thiabendazoles disclosed in JP-A-57-8542, the chlorine based disinfectants such as chlorinated sodium isocyanurate, and benzotriazole, for example, and the disinfectants disclosed in Horiguchi, The Chemistry of Biocides and Fungicides, in Killing Microorganisms, Biocidal and Fungicidal Techniques published by the Health and Hygiene Technology Society, and in A Dictionary of Biocides and Fungicides published by the Japanese Biocide and Fungicide Society, can also be used in this connection.

The pH of the washing water when processing photosensitive materials in accordance with the present invention is from 4 to 9, and preferably from 5 to 8. The washing water temperature can vary depending on the nature and application of the photosensitive material but, in general, a temperature within the range from 15° C to 45° C, and preferably within the range from 25° C to 40° C, is generally used. Moreover, the photosensitive materials of the invention can be processed directly in a stabilizing bath instead of being subjected to a water wash as described above. The known methods disclosed in JP-A-57-8543, JP-A-58-14834 and JP-A-60-220345 can be used for a stabilization process of this type.

Furthermore, in some cases a stabilization process is carried out following the above-described water washing process, and the stabilizing baths which contain dye stabilizing agents and surfactants which are used as final baths with color photosensitive materials for camera use are an example of such a process. Aldehydes such as formaldehyde and glutaraldehyde, N-methylol compounds, hexamethylenetetramine and aldehyde/bisulfite addition compounds can be used, for example, as dye stabilizing agents. Furthermore, non-ionic surfactants are preferred for the surfactant, and alkyl phenyl ether based compounds and silicon based compounds are especially preferred. Various chelating agents and fungicides can also be added to these stabilizing baths.

The overflow which accompanies replenishment of the above described water washing or stabilizing baths can be reused in other processes, such as the de-silvering process for example.

Concentration correction with the addition of water is desirable in cases where the above described processing baths become concentrated due to evaporation when processing in an automatic processor, for example.

Color developing agents can be incorporated into the silver halide color photosensitive material of the present invention to simplify and speed up processing. The incorporation of various color developing agent precursors is preferred. For example, the indoaniline based compounds disclosed in U.S. Patent 3,342,597, the Shiff's base type compounds disclosed in U.S. Patent 3,342,599, Research Disclosure No. 14850 and ibid., No. 15159, the aldol compounds disclosed in Research Disclosure No. 13924, the metal complex salts disclosed in U.S. Patent 3,719,492 and the urethane based compounds disclosed in JP-A-53-135628 can be used for this purpose.

Various 1-phenyl-3-pyrazolidones may be incorporated, as required, into the silver halide color photosensitive materials of the present invention to accelerate color development. Typical compounds are disclosed, for example, in JP-A-56-64339, JP-A-57-144547 and JP-A-58-115438.

The various processing baths employed in the present invention are used at a temperature of from 10°C to 50°C. The standard temperature is generally from 33°C to 38°C, but accelerated processing and shorter processing times can be achieved at higher temperatures while, on the other hand, increased picture quality and better processing bath stability can be achieved at lower temperatures. Furthermore, processing using hydrogen peroxide intensification or cobalt intensification as disclosed in West German Patent 2,226,770 or U.S. Patent 3,674,499 can be carried out in order to economize on silver in the photosensitive material.

The color photographic photosensitive materials for camera use of the present invention comprise, on a support, at least one blue sensitive silver halide emulsion layer, at least one green sensitive silver halide emulsion layer and at least one red sensitive silver halide emulsion layer, but no particular limitation is imposed upon the number of or order of these silver halide emulsion layers and the non-photosensitive layers present. Typically, silver halide photographic photosensitive materials have, on a support, at least one photosensitive layer comprising a plurality of silver halide layers which have essentially the same color sensitivity but different photographic speeds, the photosensitive layer being a photosensitive layer unit which is color sensitive to blue light, green light or red light. In multi-layer silver halide color photographic materials, the arrangement of the unit photosensitive layers generally involves the positioning of the layers in the order, from the support side, of red sensitive layer, green sensitive layer, and blue sensitive layer. However, this order may be varied, as required, and the layers may be arranged such that a layer which has a different color sensitivity is sandwiched between layers which have the same color sensitivity.

Various non-photosensitive layers, such as intermediate layers, may be positioned between the silver halide photosensitive layers, and as uppermost and lowermost layers.

The intermediate layers may contain couplers and DIR compounds such as those disclosed in the specifications of JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037 and JP-A-61-20038, and they may also contain anti-color mixing compounds, ultraviolet absorbers and anti-staining agents generally used.

The plurality of silver halide emulsion layers each photosensitive layer unit is preferably a double layer structure comprising a high speed emulsion layer and a low speed emulsion layer as disclosed in West German Patent 1,121,470 or British Patent 923,045. Generally, arrangements in which the photographic speed is lower in the layer closer to the support are preferred, and nonphotosensitive layers may be established between each of the silver halide emulsion layers. Furthermore, the low speed layers may positioned on the side furthest away from the support and the high speed layers may be positioned on the side closest to the support as disclosed, for example, in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541 and JP-A-62-206543.

Mere specifically, the arrangement may be, from the side furthest from the support, low speed blue sensitive layer (BL)/high speed blue sensitive layer (BH)/high speed green sensitive layer (GH)/low speed green sensitive layer (GL)/high speed red sensitive layer (RH)/low speed red sensitive layer (RL), or

BH/BL/GL/GH/RH/RL, or BH/BL/GH/GL/RL/RH.

Furthermore, the layers can be arranged in the order, from the side furthest from the support, of blue sensitive layer/GH/RH/GL/RL as disclosed in JP-B-55-34932. Furthermore, the layers can also be arranged in the order, from the side farthest from the support, of blue sensitive layer/GL/RL/GH/RH, as disclosed in the specifications of JP-A-56-25738 and JP-A-62-63936.

Furthermore, arrangements in which there are three layers which have different speeds with the speed falling towards the support with a high speed silver halide emulsion layer at the top, a silver halide emulsion layer which has a lower speed than the above-described layer as an intermediate layer and a silver halide emulsion layer which has a lower speed than the intermediate layer as a bottom layer, as disclosed in JP-B-49-15495, can also be used. In structures of this type which have three layers with different speeds, the layers in a layer of the same color sensitivity may be arranged in the order, from the side furthest from the support, of intermediate speed emulsion layer/high speed emulsion layer/low speed emulsion layer, as disclosed in the specification of JP-A-59-202464.

Furthermore, the layers can be arranged in the order high speed emulsion layer/low speed emulsion layer/intermediate speed emulsion layer, or low speed emulsion layer/intermediate speed emulsion layer/high speed emulsion layer for example.

Furthermore, the arrangement may be varied in the ways indicated above where there are four or more layers as well.

Arrangements in which donor layers (CL) which have a laminating effect and of which the spectral sensitivity distribution differs from that of the principal photosensitive layer such as BL, GL, RL etc. are adjacent to, or in the proximity of, the principal photosensitive layers, as disclosed in U.S. Patents 4,663,271, 4,705,744 and 4,707,436, JP-A-62-106448 and JP-A-63-89580, are preferred for improving color reproduction.

As described above, various layer structures and arrangements can be selected respectively depending on the purpose of the photosensitive material.

All of these layer arrangements can be used in the color photosensitive materials in the present invention, but color photosensitive materials of which the dry film thickness of all the structural layers (photographic structural layers) except the support, the under-layer of the support and the backing layer is 23.0 μm or less is preferred in the present invention.

It is thought that this is because the color developing agents which are taken up into these layers of the color photosensitive material during processing and the various coated components can be washed out more easily in the color development and subsequent processes as the film thickness is reduced.

Moreover, the lower limiting value for the film thickness specification is preferably such that the film thickness is reduced within a range in which there is no pronounced loss of performance of the photosensitive materials. The lower limit for the total dry film thickness of the structural layers other than the support and the under-layer of the support of the sensitive material is preferably 12.0 μm, and the lower limit for the total dry film thickness of the structural layer which is established between the photosensitive layer which is located closest to the support and the under-layer of the support is preferably 1.0 μm.

Furthermore, reduction of the layer thickness can be achieved with the photosensitive layers and the nonphotosensitive layers.

The film thickness of a multi-layer color photosensitive material in the present invention is measured using the method described below.

The sensitive material which is to be measured is stored for 7 days after preparation under conditions of 25 °C and 50% RH. First of all, the total thickness of the sensitive material is measured and then the thickness is measured again after removing the coated layers from the support and the difference is taken to be the total film thickness of the coated layers except for the support of the sensitive material. The measurement of this thickness can be achieved using a film thickness gauge of the contact type with a voltage conversion element for example (Anritsu Electric Co. Ltd., K-402B Stand.) Moreover, the removal of the coated layer from the support can be achieved using an aqueous solution of sodium hypochlorite.

Next, a cross sectional photograph of the above mentioned sensitive material is taken using a scanning electron microscope (magnification preferably at least 3,000 times), the total thickness and the thickness of each layer on the support is measured and the thickness of each layer can then be calculated as a proportion of the measured value of the total thickness obtained beforehand with the film thickness gauge (the absolute value of the thickness as measured).

The swelling factor of the sensitive material in this present invention is preferably from 50 to 200%, and most desirably from 70 to 150%. The swelling factor can be calculated from the equilibrium swelled film thickness in water at 25 °C and the total dry film thickness at 25 °C, 55% RH using the following expression:

$$\frac{\text{Equilibrium Swelled Film Thickness} - \text{Total Dry Film Thickness}}{\text{Total Dry Film Thickness}} \times 100\ (\%)$$

The amount of residual color developing agent increases when the swelling factor varies from the above mentioned numerical values and there is an adverse effect on photographic performance, on the image, on the desilvering properties, and on the properties of the film such as the film strength, for example.

Moreover, the film swelling rate $T_{1/2}$ of the photosensitive material in the present invention is preferably not more than 15 seconds and most preferably not more than 9 seconds. Here, the film thickness $T_{1/2}$ can be measured using methods well known in the art. For example, measurements can be made using a swellometer of the type described by A. Green in Photogr. Sci. Eng., Volume 19, Number 2, pages 124 - 129, and $T_{1/2}$ is defined as the time taken to reach half the saturated film thickness, taking 90% of the maximum swelled film thickness arising on processing the material for 3 minutes 15 seconds in a color developer at 30° C as the saturated film thickness.

Preferred silver halides for the photographic emulsion layers of a color photographic photosensitive material for camera use which is used in the present invention are silver iodobromides, silver iodochlorides and silver iodochlorobromides which contain not more than about 30 mol% of silver iodide. Most preferably they are silver iodobromides which contain from about 2 mol% to about 25 mol% of silver iodide.

The silver halide grains in the photographic emulsion may have a regular crystalline form such as a cubic, octahedral or tetradecahedral form, an irregular crystalline form such as a spherical or plate-like form, a form which has crystal defects such as twinned crystal planes, or a form which is a composite of these forms.

The grain size of the silver halide may be very fine, about 0.2 μm or less or large with a projected area diameter of up to about 10 μm. Moreover, the emulsions may be poly-disperse emulsions or mono-disperse emulsions.

The silver halide photographic emulsions which can be used in the present invention can be prepared, for example, using the methods disclosed in Research Disclosure (RD) No. 17643 (December, 1978), pages 22 - 23, "I. Emulsion Preparation and Types", and Research Disclosure No. 18716 (November 1979), page 648, in P. Glafkides, Chimie et Physique Photopraphique, published by Paul Montel, 1967, in G.F. Duffin, Photographic Emulsion Chemistry, published by Focal Press, 1966, and in V.L. Zelikmann et al., Making and Coating Photographic Emulsions, published by Focal Press, 1964.

The mono-dispersions disclosed, for example, in U.S. Patents 3,574,628 and 3,655,394, and British Patent 1,413,748 are also desirable.

Furthermore, tabular grains which have an aspect ratio of at least about 5 can be used in the present invention. Tabular grains can be prepared easily using the methods described, for example, in Gutoff, Photographic Science and Engineering, Volume 14, pages 248 - 257 (1970), and in U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520, and British Patent 2,112,157.

The crystal structure may be uniform, or the interior and exterior parts of the grains may have different halogen compositions, or the grains may have a layer-like structure. Moreover, silver halides which have different compositions may be joined with an epitaxial junction or they may be joined with compounds other than silver halides, such as silver thiocyanate or lead oxide, for example.

Furthermore, mixtures of grains which have various crystalline forms can be used.

The silver halide emulsions used generally are subjected to physical ripening, chemical ripening and spectral sensitization. Additives which are used for these purposes are disclosed in Research Disclosure No. 17643 and ibid., No. 18716, and these disclosures are summarized in the table below.

Known photographically useful additives which can be used in the present invention are also disclosed in the two Research Disclosures referred to above, and these disclosures are also summarized in the table below.

	Type of Additive	RD 17643	RD 18716
1.	Chemical Sensitizers	Page 23	Page 648, right col.
2.	Speed Increasing Agents		As above
3.	Spectral Sensitizers and Super-Sensitizers	Pages 23 - 24	Pages 648 right col. to 649 right col.
4.	Whiteners	Page 24	
5.	Anti-Foggants and Stabilizers	Pages 24 - 25	Page 649, right col.
6.	Light Absorbers, Filter Dyes and UV Absorbers	Pages 25 - 26	Pages 649, right col. to 650, left col.
7.	Anti-Staining Agents	Page 25, right col.	Page 650, right left-right cols.
8.	Dye Image Stabilizers	Page 25	
9.	Film Hardening Agents	Page 26	Page 651, left col.
10.	Binders	Page 26	As above
11.	Plasticizers, Lubricants	Page 27	Page 650, right col.
12.	Coating Promotors, Surfactants	Pages 26 - 27	As above
13.	Anti-Static Agents	Page 27	As above

Furthermore, the addition of compounds which can react with and fix formaldehyde disclosed in U.S. Patents 4,411,987 and 4,435,503 to the photosensitive material is preferred to prevent a deterioration of photographic performance due to formaldehyde gas.

Various color couplers can be used in the present invention, and specific examples are disclosed in the patents cited in Research Disclosure (RD) No. 17643, sections VII-C - G.

Those 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 3,725,067, Research Disclosure No. 24220 (June 1984), JP-A-60-33552, Research Disclosure No. 24230 (June 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, JP-A-60-185951, U.S. Patents 4,500,630, 4,540,654 and 4,556,630, and International Patent WO 88/04795 are especially preferred.

Phenol 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 Patent Laid Open 3,329,729, European Patents 121,365A and 249,453A, U.S. Patents 3,446,622, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212 and 4,296,199, and JP-A-61-42658 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, 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 for unwanted absorption of colored dyes by means of fluorescent dyes which are released on coupling as disclosed in U.S. Patent 4,774,181, and couplers which have, as leaving groups, dye precursor groups which can form dyes on reaction with the developing agent disclosed in U.S. Patent 4,777,120 is also preferred.

The couplers disclosed in U.S. Patent 4,366,237, British Patent 2,125,570, European Patent 96,570 and West German Patent (Laid Open) 3,234,533 are preferred as couplers where the colored dyes formed have a suitable degree of diffusibility.

Typical examples of polymer dye forming couplers are 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 Research Disclosure 17643, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, JP-A-63-37346, JP-A-63-37350 and U.S. Patents 4,248,962 and 4,782,012 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 correspondence to the image formed during development.

Other compounds which can be used in photosensitive materials of this present invention include the competitive couplers disclosed, for example, in U.S. Patent 4,130,427, the poly-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 which release dyes whose color is restored after elimination disclosed in European Patent 173,302A, 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 which release fluorescent dyes disclosed in U.S. Patent 4,774,181.

The couplers which are used in the present invention can be introduced into the photosensitive material using a variety of known dispersion methods.

Examples of high boiling point solvents which can be used in the oil in water dispersion method are disclosed, for example, in U.S. Patent 2,322,027. Specific examples of high boiling point organic solvents which have a boiling point of at least 175 °C at normal pressure which can be used in the oil in water dispersion method include phthalic acid esters (for example, dibutyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-tert-amylphenyl)phthalate, bis(2,4-di-tert-amylphenyl)-isophthalate and bis(1,1-diethylpropyl)phthalate), phosphate or phosphonate esters (for example, triphenyl phosphate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tri-dodecyl phosphate, tri-butoxyethyl phosphate, tri-chloropropyl phosphate and di-2-ethylhexyl phenyl phosphonate), benzoic acid esters (for example, 2-ethylhexyl benzoate, dodecyl benzoate, 2-ethylhexyl-p-hydroxybenzoate), amides (for example, N,N-diethyldodecanamide, N,N-diethyllaurylamide and N-tetradecylpyrrolidone), alcohols or phenols (for example, iso-stearyl alcohol and 2,4-di-tert-amylphenol), aliphatic carboxylic acid esters (for example, bis(2-ethylhexyl)sebacate, dioctyl azelate, glycerol tributyrate, iso-stearyl lactate and trioctyl citrate), aniline derivatives (for example, N,N-dibutyl-2-butoxy-5-tert-octylaniline) and hydrocarbons (for example, paraffins, dodecylbenzene and di-isopropylnaphthalene). Furthermore, organic solvents which have a boiling point of about 30 °C or more and preferably of at least 50 °C, but about 160 °C or less can be used as auxiliary solvents. Typical examples of these auxiliary solvents include ethyl acetate, butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethyl acetate and dimethylformamide.

Specific examples of the processes and effects of the latex dispersion method and of latexes for loading purposes are disclosed, for example, in U.S. Patent 4,199,363, and West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

Furthermore, these couplers can be loaded into a loadable latex in the presence or absence of the above-described high boiling point organic solvents (for example, as disclosed in U.S. Patent 4,203,716), or they can be dissolved in a water insoluble but organic solvent soluble polymer and emulsified and dispersed in an aqueous hydrophilic colloid solution.

Moreover, use of the homopolymers or copolymers disclosed on pages 12 - 30 of the specification of International Patent WO88/00723 is preferred. The use of acrylamide based polymers is especially preferred from the viewpoint of dye stabilization.

The addition to the color photosensitive materials in the present invention of various fungicides and biocides, such as 1,2-benzisothiazolin-3-one, n-butyl p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol and 2-(4-thiazolyl)benzimidazole, as disclosed in JP-A-63-257747, JP-A-62-272248 and JP-A-1-80941 is preferred.

Suitable supports which can be used in the present invention are disclosed, for example, on page 28 of Research Disclosure No. 17643, and from the right hand column of page 647 to the left hand column of page 648 of Research Disclosure No. 18716.

This present invention is applicable to a variety of color photosensitive materials. Its application to color negative films for general and cinematographic purposes and to color reversal films for slides and television purposes is especially preferred.

The invention is described in greater detail below by reference to the following examples but the present invention is not to be construed as being limited to these examples. Unless otherwise indicated herein, all parts, percents, ratios and the like are by weight.

EXAMPLE 1

A multi-layer color photosensitive material was prepared by lamination coating of each of the layers of whose composition is shown below on a triacetylcellulose film support on which an under-layer had been established.

Composition of the Photosensitive Layer

The numerical value corresponding to each component below indicates the coated weight in g/m^2. In the case of the silver halides this is shown as the coated weight as silver. Furthermore, with the sensitizing dyes, the coated weights are shown as mol per mol of silver halide in the same layer.

Sample 201

First Layer Anti-halation Layer

Black Colloidal Silver	as silver	0.18
Gelatin		0.40

Second Layer Intermediate Layer

2,5-Di-tert-pentadecylhydroquinone	0.18
EX-1	0.07
EX-3	0.02
EX-12	0.002
U-1	0.06
U-2	0.08
U-3	0.10
HBS-1	0.10
HBS-2	0.02
Gelatin	1.04

Third Layer First Red Sensitive Emulsion Layer

Mono-disperse Silver Iodobromide Emulsion (6 mol% AgI, average grain size 0.6 μm, variation coefficient for 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}
Sensitizing Dye IV		4.0×10^{-5}
EX-2		0.350
HBS-1		0.005

EX-10		0.020
Gelatin		1.20

Fourth Layer Second Red Sensitive Emulsion Layer

Tabular Silver Iodobromide Emulsion (10 mol% AgI, average grain diameter 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}
Sensitizing Dye IV		3.0×10^{-5}
EX-2		0.400
EX-3		0.050
EX-10		0.015
Gelatin		1.30

Fifth Layer Third Red Sensitive Emulsion Layer

Silver Iodobromide Emulsion (16 mol% AgI, 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}
EX-3		0.240
EX-4		0.120
HBS-1		0.22
HBS-2		1.10

Gelatin		1.63

Sixth Layer Intermediate Layer

EX-5		0.040
HBS-1		0.020
EX-12		0.004
Gelatin		0.80

Seventh Layer First Green Sensitive Emulsion Layer

Tabular Silver Iodobromide Emulsion (6 mol% AgI, average grain diameter 0.6 μm, average aspect ratio 6.0, average grain 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		0.260
EX-1		0.021
EX-7		0.030
EX-8		0.025
HBS-1		0.100
HBS-4		0.010
Gelatin		0.75

Eighth Layer Second Green Sensitive Emulsion Layer

Mono-disperse Silver Iodobromide Emulsion (9 mol% AgI, 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		0.180
Ex-8		0.010
EX-1		0.008
EX-7		0.012
HBS-1		0.160
HBS-4		0.008
Gelatin		1.10

<u>Ninth layer</u> Third Green Sensitive Emulsion Layer

Silver Iodobromide Emulsion (12 mol% AgI, average grain size 1.0 μm)	as silver	1.2
Sensitizing Dye V		3.5×10^{-5}
Sensitizing Dye VI		8.0×10^{-5}
Sensitizing Dye VII		3.0×10^{-4}
EX-6		0.065
EX-11		0.030
EX-1		0.025
HBS-1		0.25
HBS-2		0.10
Gelatin		1.74

<u>Tenth Layer</u> Yellow Filter Layer

Yellow Colloidal Silver	as silver	0.05
EX-5		0.08
HBS-3		0.03

Gelatin		0.95

Eleventh layer First Blue Sensitive Emulsion Layer

Tabular Silver Iodobromide Emulsion (6 mol% AgI, average grain diameter 0.6 µm, average aspect ratio 5.7, average grain thickness 0.15 µm)	as silver	0.24
Sensitizing Dye VIII		3.5×10^{-4}
EX-9		0.85
EX-8		0.12
HBS-1		0.28
Gelatin		1.28

Twelfth Layer Second Blue Sensitive Emulsion Layer

Mono-disperse Silver Iodobromide Emulsion (10 mol% AgI, 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		0.20
EX-10		0.015
HBS-1		0.03
Gelatin		0.46

Thirteenth layer Third Blue Sensitive Emulsion Layer

Silver Iodobromide Emulsion (14 mol% AgI, average grain size 1.3 µm)	as silver	0.77
Sensitizing Dye VIII		2.2×10^{-4}
EX-9		0.20
HBS-1		0.07

Gelatin		0.69

Fourteenth Layer First Protective Layer

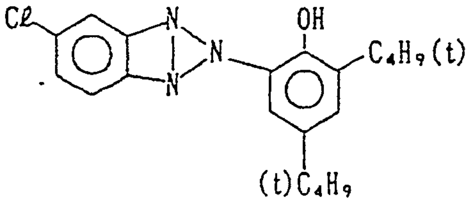
Silver Iodobromide Emulsion (1 mol% AgI, average grain size 0.07 μm,)	as silver	0.5
U-4		0.11
U-5		0.17
HBS-1		0.90
Gelatin		1.00

Fifteenth Layer Second Protective Layer

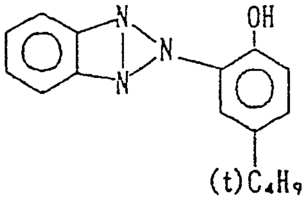
Poly(methyl acrylate) Particles (diameter about 1.5 μm)	0.54
S-1	0.15
S-2	0.05
Gelatin	0.72

In addition to the components shown above, Gelatin Hardening Agent H-1 and surfactant were added to each layer.

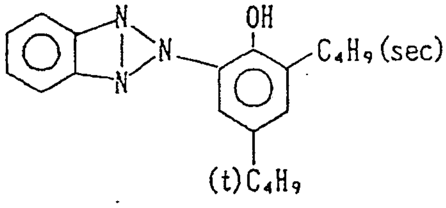
U-1



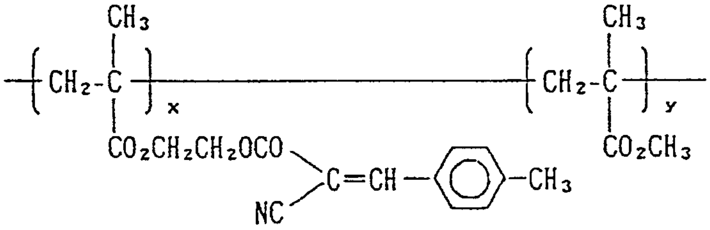
U-2



U-3

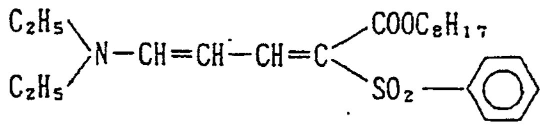


U-4

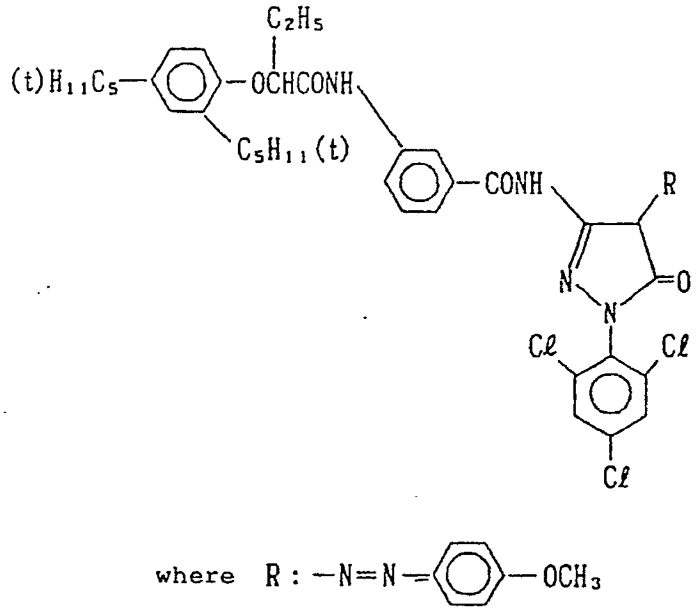


[$x/y = 7/3$ (by weight)]

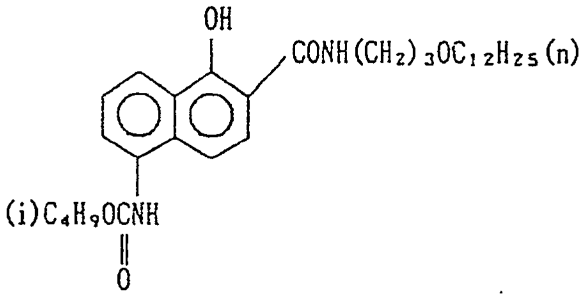
U-5


C₂H₅
C₂H₅
N—CH=CH—CH=C
COOC₈H₁₇
SO₂

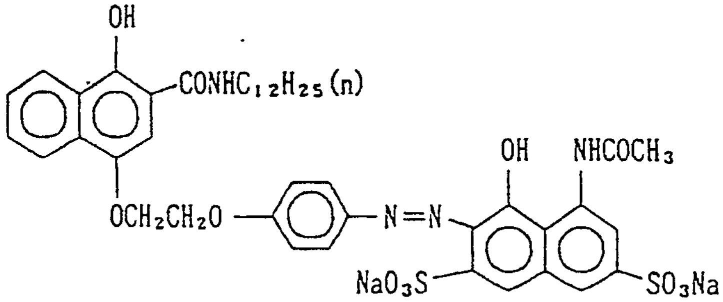
EX-1


C₂H₅
(t)H₁₁C₅
OCHCONH
C₅H₁₁(t)
CONH
R
N
N
O
Cℓ
Cℓ
Cℓ
where R : —N=N—
OCH₃

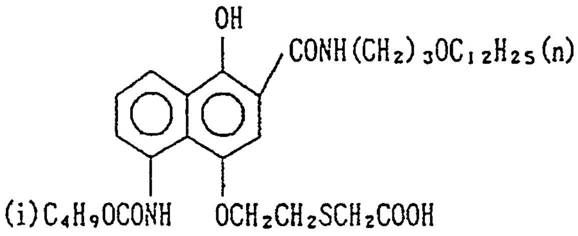
EX-2


OH
CONH(CH₂)₃OC₁₂H₂₅(n)
(i)C₄H₉OCNH
O

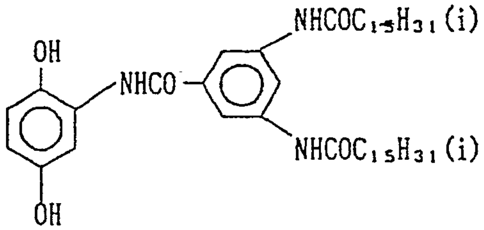
EX-3


OH
CONHC12H25(n)
OH
NHCOCH3
OCH2CH2O
N=N
NaO3S
SO3Na

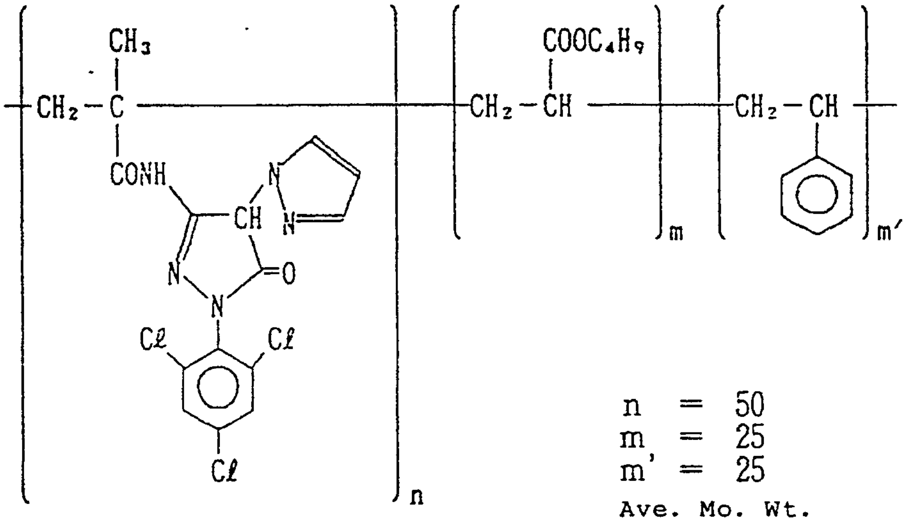
EX-4


OH
CONH(CH2)3OC12H25(n)
(i)C4H9OCONH
OCH2CH2SCH2COOH

EX-5

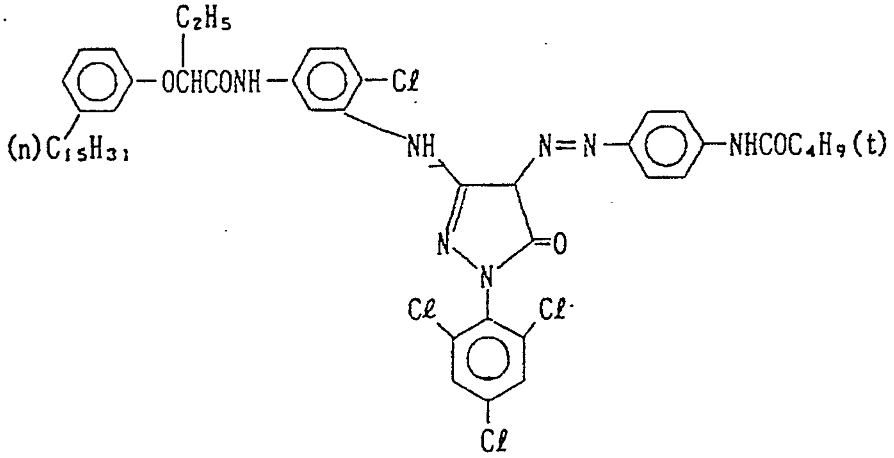

NHCOC15H31(i)
OH
NHCO
NHCOC15H31(i)
OH

EX-6

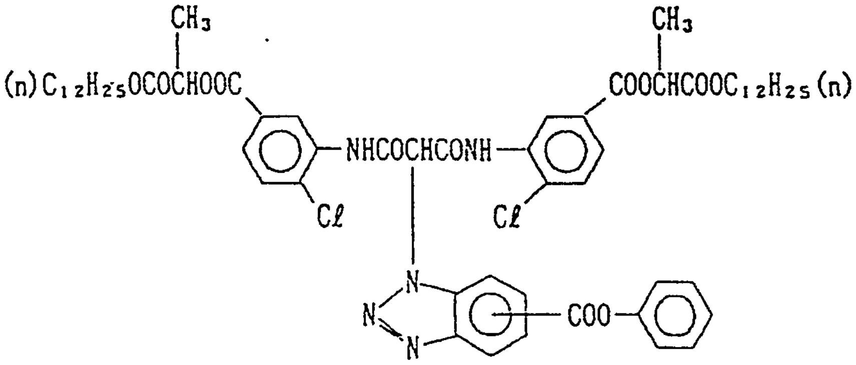


n = 50
m = 25
m' = 25
Ave. Mo. Wt.
30,000

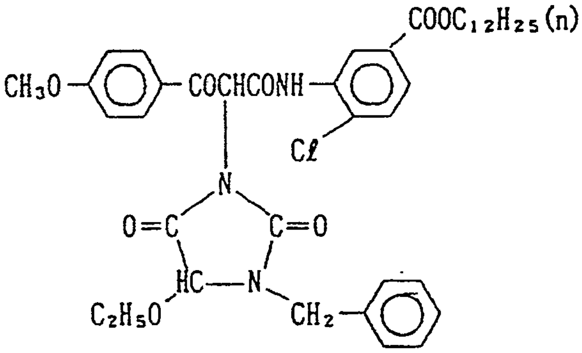
EX-7



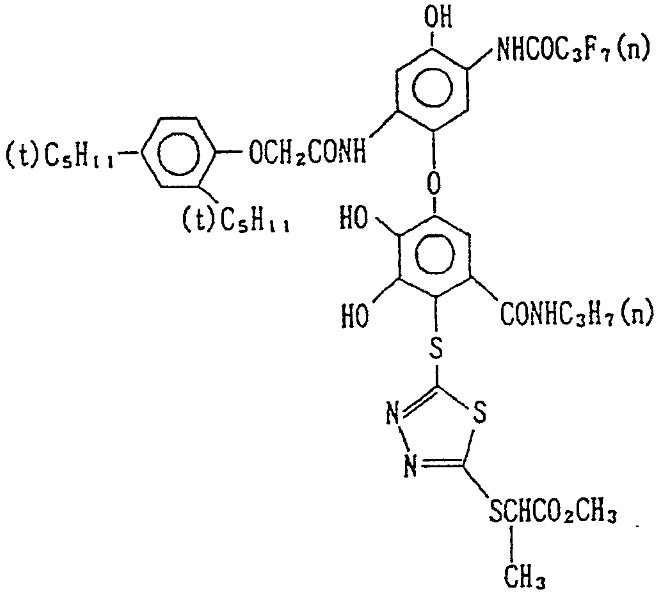
EX-8



EX-9



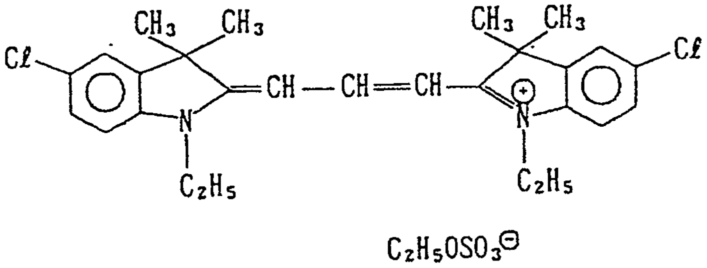
EX-10



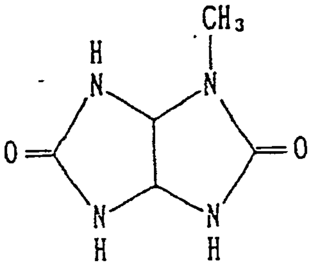
EX-11 ; Same as EX-1

but R : —H

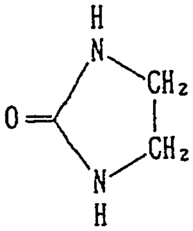
EX-12



S-1

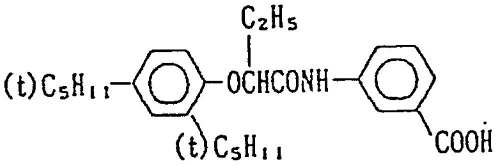


S-2

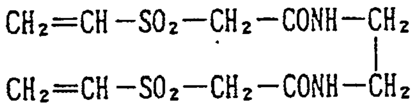


HBS-1 ; Tricresyl phosphate
HBS-2 ; Dibutyl phthalate
HBS-3 ; Bis(2-ethylhexyl)phthalate

HBS-4

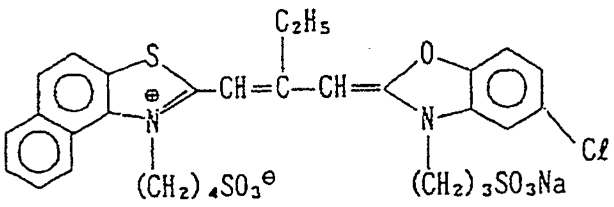


H－1

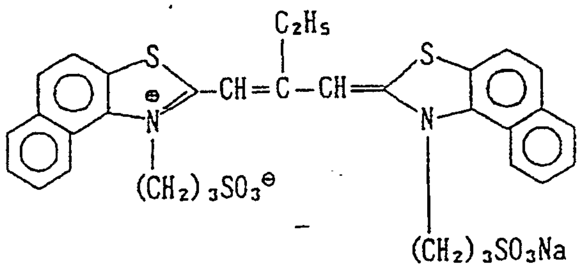


$$\begin{array}{l} CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \end{array}$$

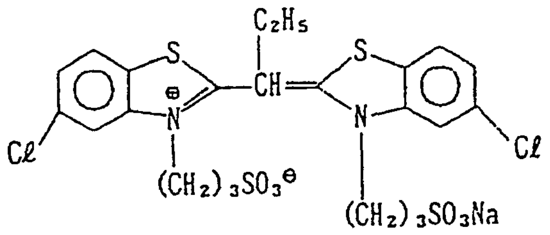
Sensitizing Dye I



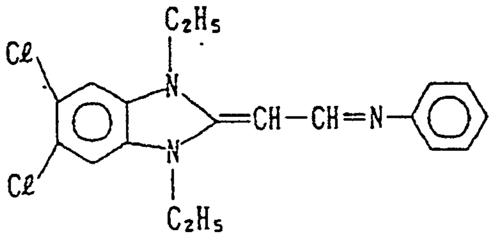
Sensitizing Dye II



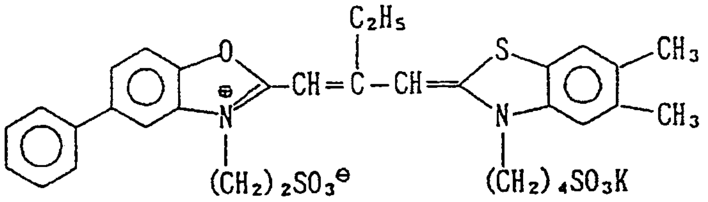
Sensitizing Dye III



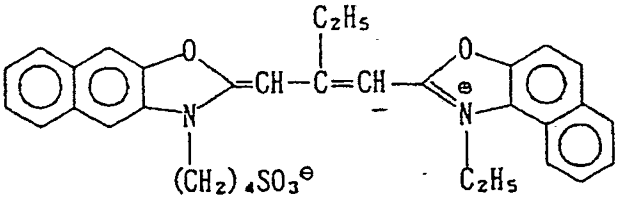
Sensitizing Dye IV



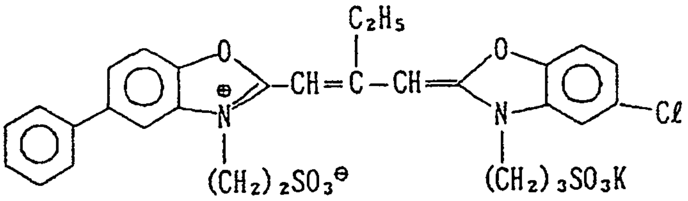
Sensitizing Dye V



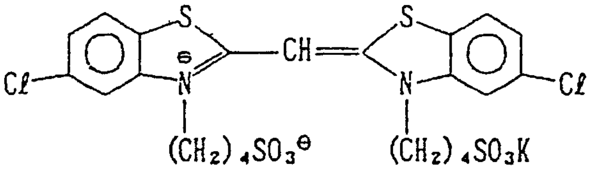
Sensitizing Dye VI



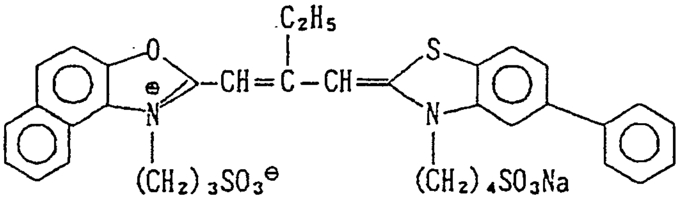
Sensitizing Dye VII



Sensitizing Dye VIII



Sensitizing Dye IX



The color film prepared in the manner described above was cut into strips of a width of 35 mm and then subjected to a standard exposure in a camera. Then the films were processed under various conditions with the processing operations shown below using a small type cine automatic processor. Each process was carried out continuously using 3.5 square meters (100 m length of 35 mm wide) of the above-described exposed film.

Processing Operations

Process	Processing Time	Temperature	Replenishment Rate*	Tank Capacity
Color Development	3 minutes 15 seconds	38.0°C	570 ml	1 liter
Bleach	45 seconds	38.0°C	130 ml	1 liter
Fix	1 minute 30 seconds	38.0°C	800 ml	1 liter
Water Wash (1)	15 seconds	38.0°C	Three Stage Counter-flow Washing System	0.5 liter
Water Wash (2)	15 seconds	38.0°C		0.5 liter
Water Wash (3)	15 seconds	38.0°C	250 ml	0.5 liter
Stabilization	15 seconds	38.0°C	200 ml	0.5 liter
Drying	1 minute 00 seconds	55°C	-	-

*: Replenishment rate per square meter of photosensitive material

Processing Conditions

Processing was carried out under conditions in which the bleaching agent in the bleach was modified in the manner indicated in Table 1 and the reverse osmosis membrane treatment apparatus as shown schematically in Figure 1 was or was not used with the water washing process.

The reverse osmosis membrane treatment involved a synthetic composite membrane made by Daicel Chemical Industries, namely a DRA-80-SW-03 model spiral module (effective membrane area 1.1 m^2), housed in a PSV-03 pressure resistant vessel made by the same company and the liquid was treated at a liquid feed pressure of 3.5 kg/cm^2 and a liquid feed rate of 1.3 liters/minute using a magnetic gear pump. The amount of permeating liquid when the reverse osmosis membrane treatment started was 230 ml/minute.

The above-described color negative film which had been subjected to a wedge exposure was then processed in the usual manner using processing liquids with which processing had been carried out in the manner described above. Then, the residual silver content of the maximum density areas and the increase in the magenta density of the minimum density areas after storage for 5 days under ambient conditions of 60° C, 70% relative humidity were measured.

The fluorescence X-ray method was used to measure the amount of residual silver and the increase in magenta density was measured using an "Exlite 310" model photographic densitometer.

The formulations of the processing baths used were as shown below.

Color Development Bath (Units: grams/liter)

	Parent Bath	Replenisher
Sodium Sulfite	4.0	5.5
Potassium Bromide	1.4	0.2
Potassium Carbonate	39.0	40.5
Diethylenetriamine Pentaacetic 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 added to pH	10.05	10.18

Bleach Bath (Units: Grams/liter)

	Parent Bath	Replenisher
Bleaching Agent (See Table 1)	0.34 mol/ℓ	0.53 mol/ℓ
Acetic Acid	35	50

Hydroxyacetic Acid (70% aq. soln.)	97	140
Ammonium Nitrate	40	60
Aqueous ammonia added to pH	3.8	2.8

Fixer Bath (Units: Grams/liter)

	Parent Bath	Replenisher
Ammonium Thiosulfate	200	350
Ammonium Sulfite	20	35
Imidazole	22	40
Ethylenediamine Tetraacetic Acid	10	18
Acetic acid added to pH	7.2	7.4

Water Washing water (Parent Bath = Replenisher)

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 strongly basic anion exchange resin ("Amberlite IRA-400", made by the Rohm and Haas Co.) to provide water of the quality indicated below.

Calcium	0.3 mg/ℓ
Magnesium	Less than 0.1 mg/ℓ
pH	6.5
Electrical Conductivity	5.0 µs/cm

Stabilizer Bath (Parent Bath=Replenisher; Units: Grams)

Formaldehyde (37% aq. soln.)	2.0 ml
Polyoxyethylene p-Monononylphenyl Ether (average degree of polymerization 10)	0.3
Ethylenediamine Tetraacetic Acid Di-sodium Salt	0.05
Water (town water)	to make 1 liter
pH	5.0 - 8.0

The results obtained are shown in Table 1.

TABLE 1

No.	Bleaching Agent	Mol. Wt. of Free Acid	Reverse Osmosis Membrane Treatment	Residual Silver (μg/cm2)	Increase in Magenta Density	Remarks
1	Ethylenediamine tetraacetic acid ferric complex salt	292.3	No	48	0.08	Comp. Ex.
2	Methylimino diacetic acid ferric complex salt	147.1	No	17	0.09	Comp. Ex.
3	Nitrilo triacetic acid ferric complex salt	191.1	No	13	0.09	Comp. Ex.
4	1,3-Diaminopropane tetraacetic acid complex salt	306.3	No	2.7	0.22	Comp. Ex.
5	1,4-Diaminobutane tetraacetic acid complex salt	320.3	No	4.3	0.24	Comp. Ex.
6	Glycol ether diamine tetraacetic acid ferric complex slat	380.4	No	4.5	0.23	Comp. Ex.
7	Triethylenetetramine hexaacetic acid ferric complex salt	494.5	No	50	0.09	Comp. Ex.

TABLE 1 (cont'd)

No.	Bleaching Agent	Mol. Wt. of Free Acid	Reverse Osmosis Membrane Treatment	Residual Silver (μg/cm^2)	Increase in Magenta Density	Remarks
8	Ethylenediamine tetraacetic acid ferric complex salt	292.3	Yes	46	0.06	Comp. Ex.
9	Methylimino diacetic acid ferric complex salt	147.1	Yes	16	0.07	Comp. Ex.
10	Nitrilo triacetic acid ferric complex salt	191.1	Yes	13	0.07	Comp. Ex.
11	1,3-Diaminopropane tetraacetic acid complex salt	306.3	Yes	2.6	0.02	Invention
12	1,4-Diaminobutane tetraacetic acid complex salt	320.3	Yes	4.0	0.02	Invention
13	Glycol ether diamine tetraacetic acid ferric complex salt	380.4	Yes	4.5	0.03	Invention
14	Triethylenetetramine hexaacetic acid ferric complex salt	494.5	Yes	51	0.09	Comp. Ex.

It is clear from the results shown in Table 1 above that with very rapid processing in which the processing time after treatment for 45 seconds in a bath which has a bleaching function up to the drying process is set at 2 minutes and 30 seconds and in which the water washing replenishment rate is reduced to 250 ml per square meter of photosensitive material, the residual silver content is very high (i.e., a desilvering failure) and there is an increase in magenta staining on storage under conditions of high temperature and humidity when ethylenediamine tetraacetic acid ferric complex salt (Test No. 1) which is generally used is employed in the bleach bath. Furthermore, there was little change in the residual silver content or in the increase in magenta staining even when the reverse osmosis membrane treatment was incorporated into such a system (Test No. 8).

Furthermore, although there was some improvement in the amount of residual silver when methylimino diacetic acid ferric complex salt was used (Test No. 2, Test No. 9) and when nitrilo triacetic acid ferric complex salt was used (Test No. 3, Test No. 10), the results were still unsatisfactory and there was still a large increase in magenta staining.

Furthermore, the amount of residual silver was very high and magenta staining greatly increased on storage under conditions of high temperature and humidity when triethylenetetramine hexaacetic acid ferric complex salt was used (Test No. 7, Test No. 14).

Furthermore, when 1,3-diaminopropane tetraacetic acid ferric complex salt, 1,4-diaminobutane tetraacetic acid ferric complex salt or glycol ether diamine tetraacetic acid ferric complex salt, in accordance with the present invention, were used without the reverse osmosis membrane treatment (Test No. 4, Test No. 5, Test No. 6), a marked decrease in the amount of residual silver occurred but even so there was a pronounced increase in magenta staining and the system could not be used in practice.

However, there was a marked decrease in the amount of residual silver, there was no de-silvering failure, and also a marked improvement occurred with less magenta staining even when processing times were very short and the water washing water replenishment rate was reduced when such systems were combined with a reverse osmosis membrane treatment (Test No. 11, Test No. 12, Test No. 13).

It is clear form the above results that the specific effect of the present invention arises only when an aminopolycarboxylic acid ferric complex salt of which the molecular weight of the aminopolycarboxylic acid is from 300 to 450 is used and the water washing water is subjected to a reverse osmosis membrane treatment when processing using an aminopolycarboxylic acid ferric complex salt as a bleaching agent.

EXAMPLE 2

A multi-layer color photosensitive material comprising the layers of the compositions shown below was prepared on a cellulose triacetate film on which an underlayer had been established.

Composition of the Photosensitive Layer

The coated weights are indicated as g.Ag/m^2 in the case of silver halides and colloidal silver, as g/m^2 in the case of the couplers, additives and gelatin, and in mol per mol of silver halide in the same layer in the case of the sensitizing dyes.

First Layer (Anti-halation Layer)

Black Colloidal Silver	0.15
Gelatin	1.5
ExM-8	0.08
UV-1	0.03
UV-2	0.06
Solv-2	0.08
UV-3	0.07

Cpd-5	6×10^{-4}

Second Layer (Intermediate Layer)

Gelatin	1.5
UV-1	0.03
UV-2	0.06
UV-3	0.07
ExF-1	0.004
Solv-2	0.07
Cpd-5	6×10^{-4}

Third Layer (First Red Sensitive Emulsion Layer)

Silver Iodobromide Emulsion (AgI 2 mol%, high internal AgI type, corresponding sphere diameter 0.3 μm, variation coefficient of corresponding sphere diameter 29%, regular crystal grain/ twinned crystal grain mixture, diameter/thickness ratio 2.5)	0.5 as silver
Gelatin	0.8
ExS-1	1.0×10^{-4}
ExS-2	3.0×10^{-4}
ExS-3	1×10^{-5}
ExC-3	0.22
ExC-4	0.02
Cpd-5	3×10^{-4}

Fourth Layer (Second Red Sensitive Emulsion Layer)

Silver Iodobromide Emulsion (AgI 4 mol%, high internal AgI type, corresponding sphere diameter	0.7 as silver

0.55 µm, variation coefficient of corresponding sphere diameter 20%, regular crystal grain/twinned crystal grain mixture, diameter/thickness ratio 1)	
Gelatin	1.26
ExS-1	1×10^{-4}
ExS-2	3×10^{-4}
ExS-3	1×10^{-5}
ExC-3	0.33
ExC-4	0.01
ExY-16	0.01
ExC-7	0.04
ExC-2	0.08
Solv-1	0.03
Cpd-5	5×10^{-4}

<u>Fifth Layer</u> (Third Red Sensitive Emulsion Layer)

Silver Iodobromide Emulsion (AgI 10 mol.%, high internal AgI type, corresponding sphere diameter 0.7 µm, variation coefficient of corresponding sphere diameter 30%, twinned crystal grain mixture, diameter/thickness ratio 2)	0.7 as silver
Gelatin	0.8
ExS-1	1×10^{-4}
ExS-2	3×10^{-4}
ExS-3	1×10^{-5}
ExC-5	0.05
ExC-6	0.06

Solv-1	0.15
Solv-2	0.08
Cpd-5	3×10^{-5}

Sixth Layer (Intermediate Layer)

Gelatin	1.0
Cpd-5	4×10^{-4}
Cpd-1	0.10
Cpd-4	1.23
Solv-1	0.05
Cpd-3	0.25

Seventh Layer (First Green Sensitive Emulsion Layer)

Silver Iodobromide Emulsion (AgI 6 mol%, high internal AgI type, corresponding sphere diameter 0.3 µm, variation coefficient of corresponding sphere diameter 28%, regular crystal grain/ twinned crystal grain mixture, diameter/thickness ratio 2.5)	0.30 as silver
Gelatin	0.4
ExS-4	5×10^{-4}
ExS-6	0.3×10^{-4}
ExS-5	2×10^{-4}
ExM-9	0.2
ExY-14	0.03
ExM-8	0.03
Solv-1	0.2
Cpd-5	2×10^{-4}

Eighth Layer (Second Green Sensitive Emulsion Layer)

Silver Iodobromide Emulsion (AgI 4 mol%, high internal AgI type, corresponding sphere diameter 0.55 µm, variation coefficient of corresponding sphere diameter 20%, regular crystal grain/twinned crystal grain mixture, diameter/thickness ratio 4)	0.6 as silver
Gelatin	0.8
ExS-4	5×10^{-4}
ExS-5	2×10^{-4}
ExS-6	0.3×10^{-4}
ExM-9	0.25
ExM-8	0.03
ExM-10	0.015
ExY-14	0.04
Solv-1	0.2
Cpd-5	3×10^{-4}

Ninth Layer (Third Green Sensitive Emulsion Layer)

Silver Iodobromide Emulsion (AgI 10 mol%, high internal AgI type, corresponding sphere diameter 0.7 µm, variation coefficient of corresponding sphere diameter 30%, regular crystal grain/twinned crystal grain mixture, diameter/thickness ratio 2.0)	0.85 as silver
Gelatin	1.0
ExS-4	2.0×10^{-4}
ExS-5	2.0×10^{-4}

ExS-6	0.2×10^{-4}
ExS-7	3.0×10^{-4}
ExM-12	0.06
ExM-13	0.02
ExM-8	0.02
Solv-1	0.20
Solv-2	0.05
Cpd-2	0.01
Cpd-5	4×10^{-4}

Tenth Layer (Yellow Filter Layer)

Gelatin	0.9
Yellow Colloidal Silver	0.05
Cpd-1	0.2
Solv-1	0.15
Cpd-5	4×10^{-4}

Eleventh Layer (First Blue Sensitive Emulsion Layer)

Silver Iodobromide Emulsion (AgI 4 mol%, high internal AgI type, corresponding sphere diameter 0.5 μm, variation coefficient of the corresponding sphere diameter 15%, octahedral grains)	0.4 as silver
Gelatin	1.0
ExS-8	2×10^{-4}
ExY-16	0.9
ExY-14	0.09
Solv-1	0.3

Cpd-5	4×10^{-4}

Twelfth Layer (Second Blue Sensitive Emulsion Layer)

Silver Iodobromide Emulsion (AgI 10 mol%, high internal AgI type, corresponding sphere diameter 1.3 μm, variation coefficient of the corresponding sphere diameter 25%, regular crystal grain/twinned crystal grain mixture, diameter/thickness ratio 4.5)	0.5 as silver
Gelatin	0.6
ExS-8	1×10^{-4}
ExY-16	0.12
Solv-1	0.04
Cpd-5	2×10^{-4}

Thirteenth Layer (First Protective Layer)

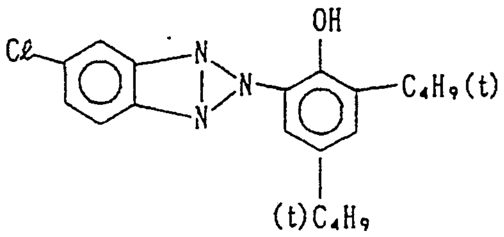
Fine-Grained Silver Iodobromide (average grain size 0.07 μm, AgI 1 mol%)	0.2
Gelatin	0.8
UV-3	0.1
UV-4	0.1
UV-5	0.2
Solv-3	0.04
Cpd-5	3×10^{-4}

Fourteenth Layer (Second Protective Layer)

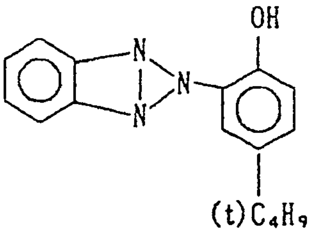
Gelatin	0.9
Poly(methyl methacrylate) Particles (diameter about 1.5 μm)	0.2
Cpd-5	4×10^{-4}
H-1	0.4

Surfactant was added to each layer as a coating promotor in addition the components indicated above. The components used in above are indicated below.

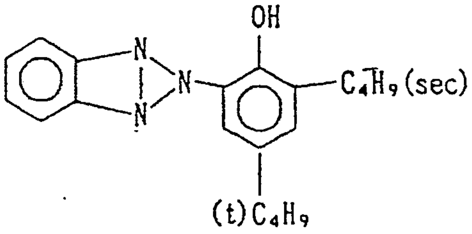
UV-1



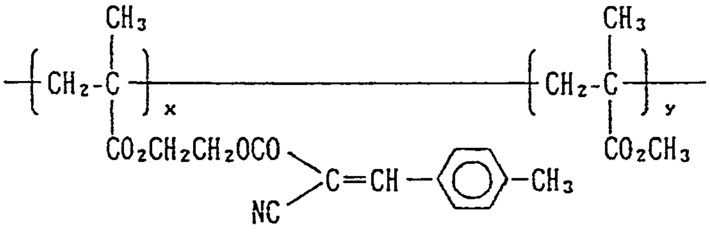
UV-2



UV-3

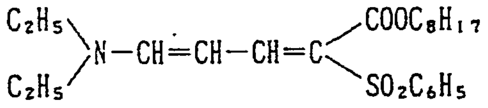


UV-4



x : y = 7 : 3 (by weight)

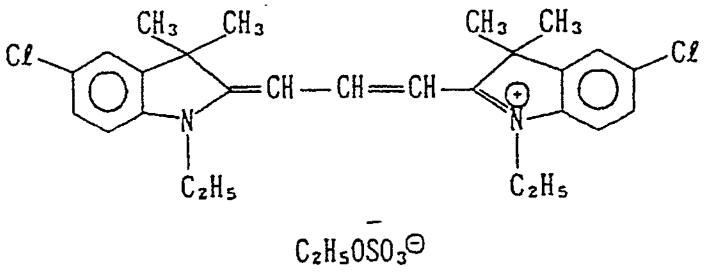
UV-5



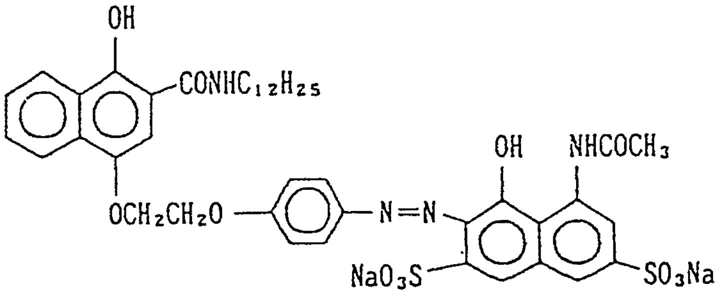
$$(C_2H_5)_2N-CH=CH-CH=C(COOC_8H_{17})(SO_2C_6H_5)$$

Solv-1 : Tricresyl phosphate
Solv-2 : Dibutyl phthalate
Solv-3 : bis(2-Ethylhexyl)phthalate

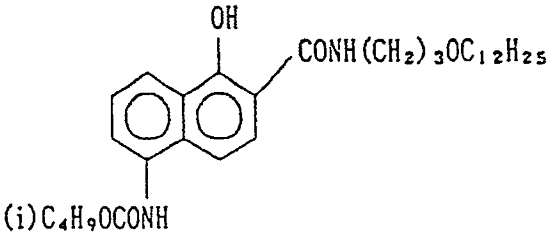
ExF-1



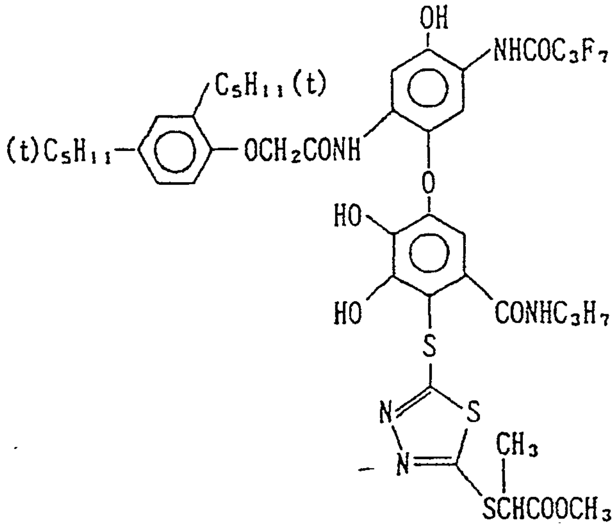
ExC-2



ExC-3



ExC-4



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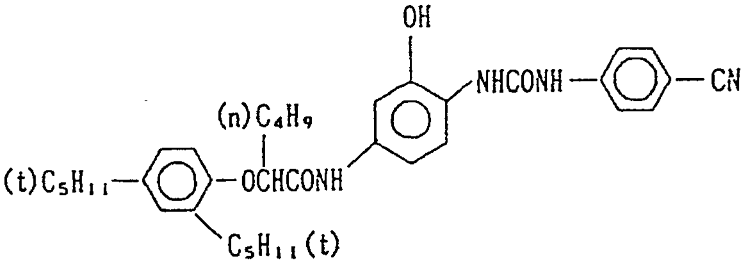
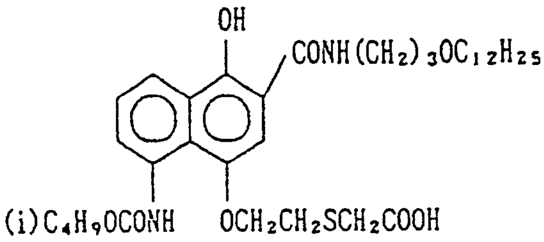


ExC-6



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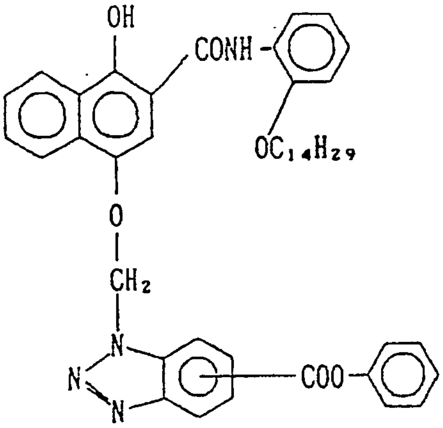
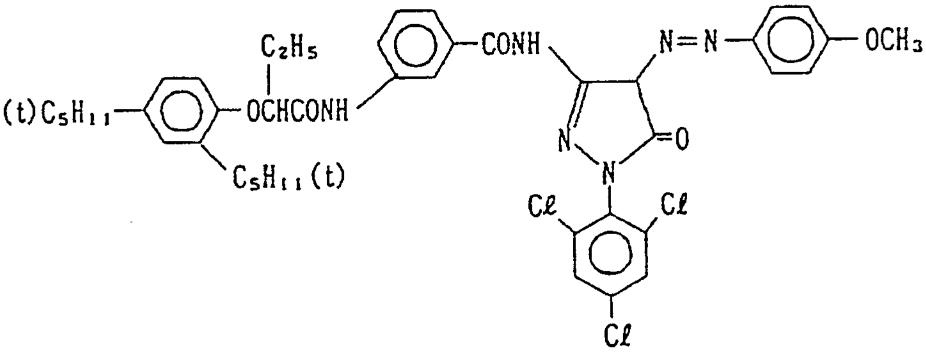
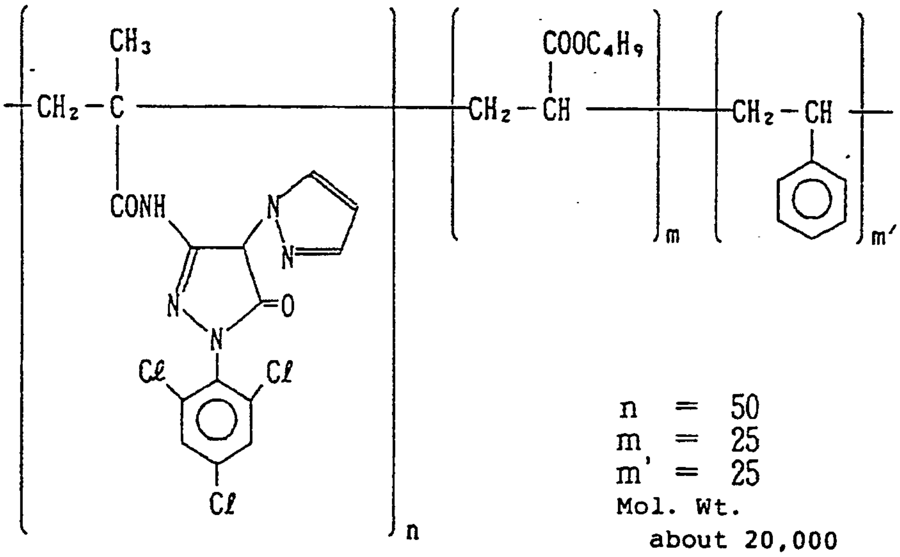


ExM-8

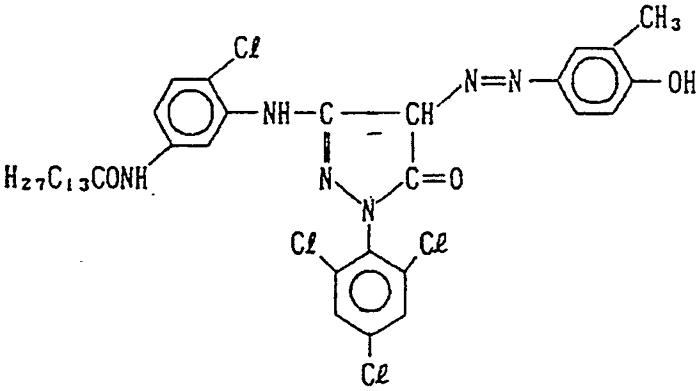


ExM-9

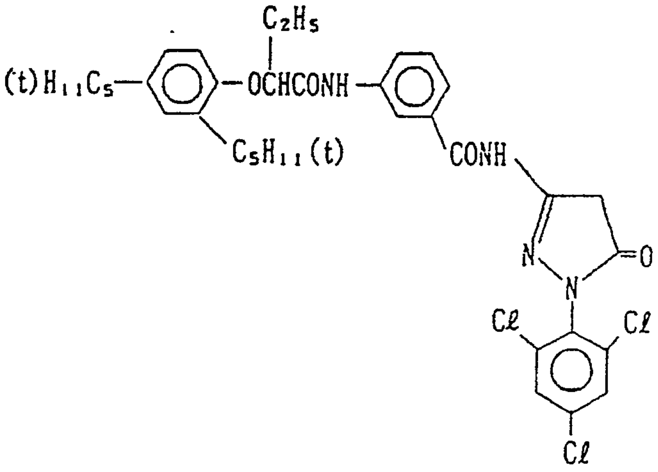


n = 50
m = 25
m' = 25
Mol. Wt.
about 20,000

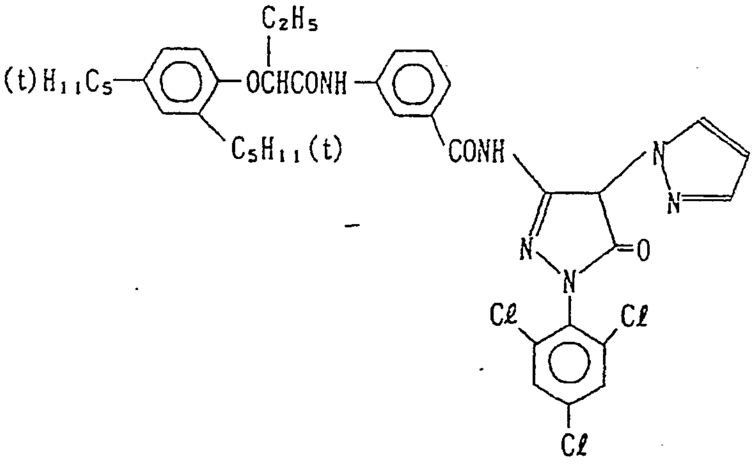
ExM-10



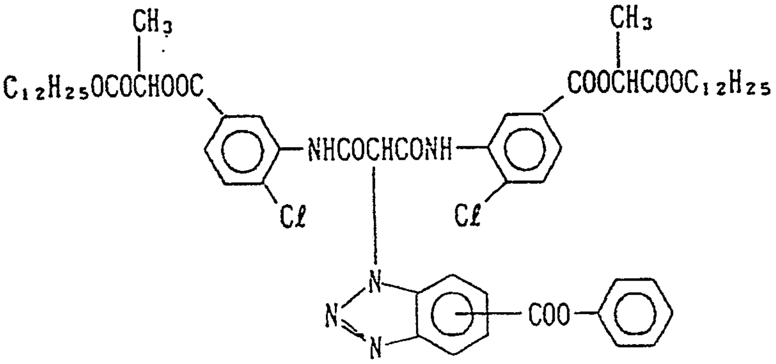
ExM−12


C2H5
(t)H11C5
OCHCONH
C5H11(t)
CONH
N
N
O
Cℓ
Cℓ
Cℓ

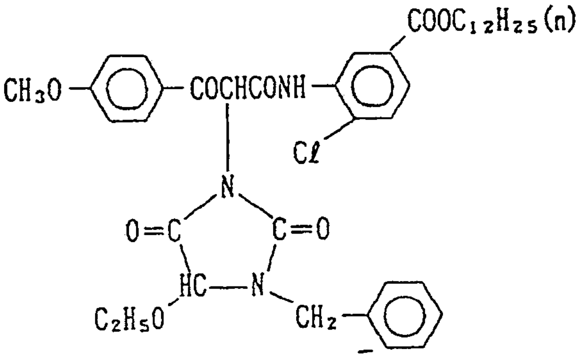
ExM−13


C2H5
(t)H11C5
OCHCONH
C5H11(t)
CONH
N
N
N
N
O
Cℓ
Cℓ
Cℓ

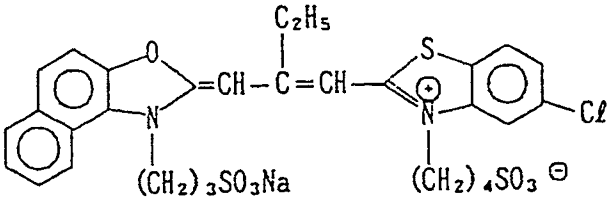
ExY−14



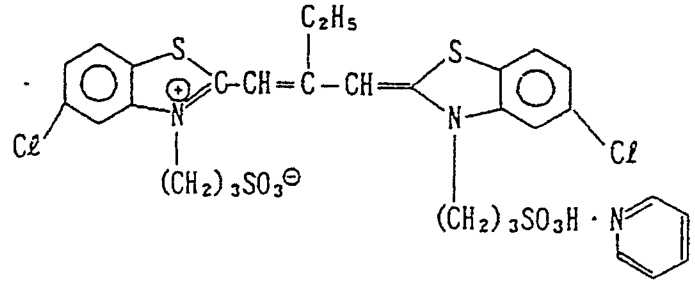
ExY−16



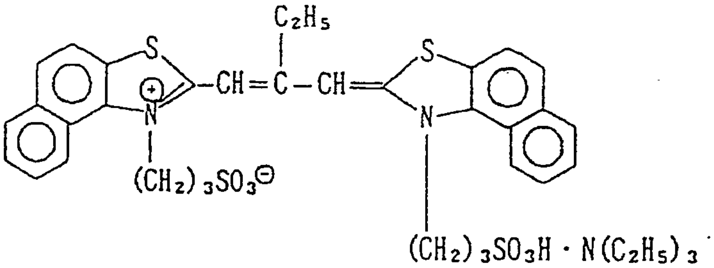
ExS−1



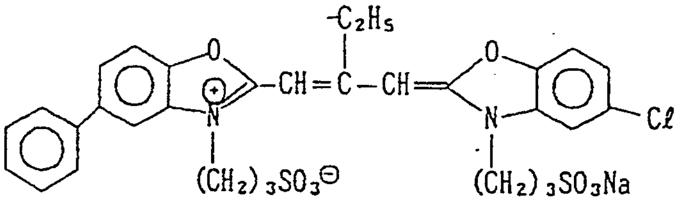
ExS－2



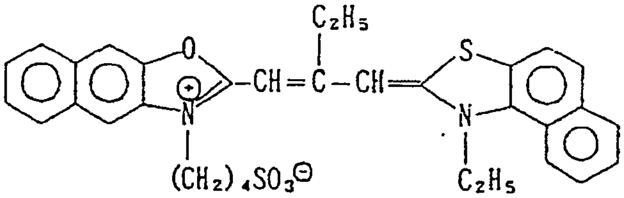
ExS－3



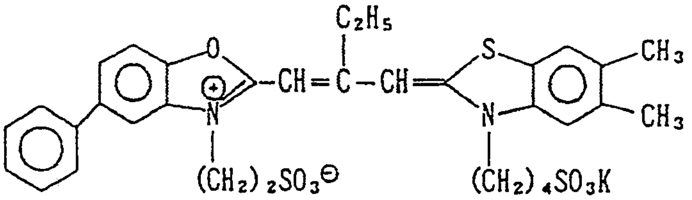
ExS－4



ExS－5



ExS-6



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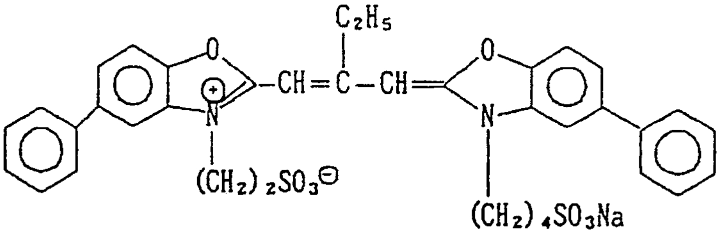
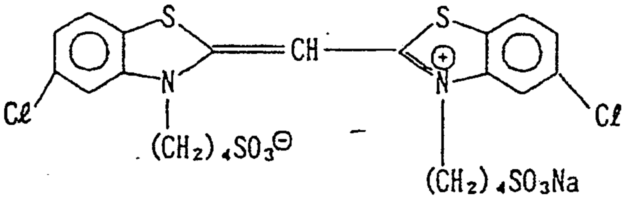
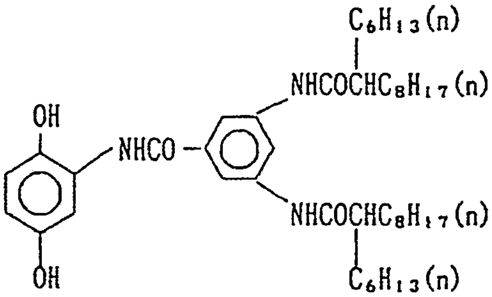


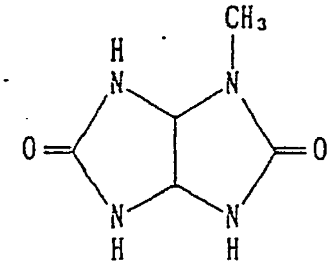
ExS-8



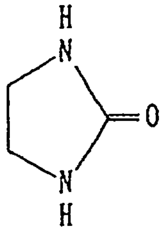
Cpd-1



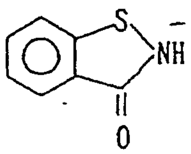
Cpd-3



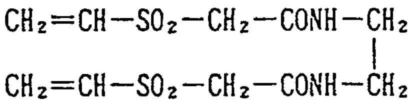
Cpd-4



Cpd-5



H-1



$$\begin{array}{l} CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \end{array}$$

The color negative film which had been prepared in the manner as described above was cut into strips of a width of 35 mm and then subjected to a standard exposure in a camera. Then, the material was processed under various processing conditions with the processing operations shown below using a small cine type automatic processor. Each processing run was continued until 3.5 m^2 (100 m long by 35 mm wide) of the a above-described exposed film had been processed.

Processing Operations

Process	Processing Time	Temperature	Replenishment Rate*	Tank Capacity
Color Development	3 minutes 15 seconds	38.0°C	570 ml	1 liter
Bleach-fix	2 minutes 30 seconds	38.0°C	800 ml	1 liter
Stabilization (1)	20 seconds	38.0°C		0.5 liter
Stabilization (2)	20 seconds	38.0°C		0.5 liter
Stabilization (3)	20 seconds	38.0°C	250 ml	0.5 liter
Drying	1 minute 00 seconds	55°C	-	-

*: Replenishment rate per square meter of photosensitive material

Processing Conditions

Processing was carried out under conditions in which the bleaching agent in the bleach-fix was changed in the manner shown in Table 2 below and the reverse osmosis membrane treatment apparatus as shown schematically in Figure 2 was or was not used in the stabilization process.

The reverse osmosis membrane treatment involved a synthetic composite membrane made by the Toray Co., namely an SU-210 model spiral module (effective membrane area 0.8 m^2), and the liquid was treated at a liquid feed pressure of 5 kg/cm^2 and a liquid feed rate of 4 liters/minute. The amount of permeating liquid when the reverse osmosis membrane treatment started was 340 ml/minute.

The above-described color negative film which had been subjected to a wedge exposure was then processed in the usual manner using the processing liquids described below with processing being carried out in the manner described above. Then the residual silver content of the maximum density areas and the increase in the magenta density of the minimum density areas after storage for 5 days under ambient conditions of 60° C, 70% relative humidity were measured. These measurements were made in the same manner as described in Example 1.

The compositions of the processing baths used were as indicated below.

Color Development Bath

Same as the color development bath in Example 1.

Bleach-fix Bath (Units: Grams/liter)

	Parent Bath	Replenisher
Bleaching Agent (See Table 2)	0.2 mol/ℓ	0.25 mol/ℓ
Benzaldehydo-o-sulfonic Acid/Disulfite Adduct	30	36
Ammonium Thiosulfate	160	200
3-Mercapto-1,2,4-triazole	1.0	1.3
pH	6.3	6.0

Stabilizer Bath (Units: Grams/liter)

	Parent Bath	Replenisher
Formaldehyde (37% aq. soln.)	1.5 ml	2.0 ml
Polyoxyethylene p-Monononylphenyl Ether (average degree of polymerization 10)	0.2	0.25
pH	6.0	6.0

The results obtained are shown in Table 2 below.

TABLE 2

No.	Bleaching Agent	Mol. Wt. of Free Acid	Reverse Osmosis Membrane Treatment	Residual Silver (µg/cm2)	Increase in Magenta Density	Remarks
21	Ethylenediamine tetraacetic acid ferric complex salt	292.3	No	13.2	0.09	Comp. Ex.
22	Diethylenetriamine pentaacetic acid ferric complex salt	393.4	No	7.1	0.15	Comp. Ex.
23	Cyclohexanediamine tetraacetic acid ferric complex salt	346.4	No	4.2	0.21	Comp. Ex.
24	1,3-Diaminopropane tetraacetic acid complex salt	306.3	No	2.3	0.23	Comp. Ex.
25	1,2-Diaminopropane tetraacetic acid	306.3	No	9.0	0.18	Comp. Ex.
26	Ethylenediamine tetraacetic acid ferric complex slat	292.3	Yes	12.8	0.07	Comp. Ex.
27	Diethylenetriamine pentaacetic acid ferric complex salt	393.4	Yes	7.3	0.02	Invention
28	Cyclohexanediamine tetraacetic acid ferric complex salt	346.4	Yes	3.5	0.22	Invention
29	1,3-Diaminopropane tetraacetic acid ferric complex salt	306.3	Yes	2.5	0.03	Invention
30	1,2-Diaminopropane tetraacetic acid	306.3	Yes	9.1	0.04	Invention

It is clear from the results shown in Table 2 above that on processing very rapidly with a stabilization processing time after processing for 2 minute 30 seconds in a bath which had a bleaching function up to the drying process of 1 minute and a low replenishment rate of 250 ml per square meter of the photosensitive material for the stabilizing bath, there was a remarkably high residual silver content and a pronounced increase in magenta staining on storage under conditions of high temperature and humidity when ethylenediamine tetraacetic acid ferric complex salt which is generally used commercially was used (Test No. 21). Furthermore, the incorporation of a reverse osmosis membrane treatment into this system (Test No. 26) had little improving effect and it could not be used in practice.

Furthermore, although there was some improvement in reduction in the amount of residual silver when diethylenetriamine pentaacetic acid ferric complex salt, cyclohexanediamine tetraacetic acid ferric complex salt, 1,3-diaminopropane tetraacetic acid ferric complex salt or 1,2-diaminopropane tetraacetic acid ferric complex salt was used in accordance with this invention (Test No. 22, Test No. 23, Test No. 24, Test No. 25), there was still a large increase in magenta staining and the system could not be used in practice.

However, there was a marked improvement in the reduction in the residual silver and there was no de-silvering failure. Also, there was a marked improvement in the reduction in the increase in magenta staining even when processing times were very short and the water washing water replenishment rate was reduced when such systems were combined with a reverse osmosis membrane treatment (Test No. 27, Test No. 28, Test No. 29, Test No. 30).

By means of the present invention, it is possible to obtain excellent images with which de-silvering failure is unlikely to occur and which are unlikely to exhibit increased magenta staining on storage under conditions of high temperature and humidity even when silver halide color photographic photosensitive materials for camera use are processed very rapidly with a processing time after processing in a bath which has a bleaching function up to the drying process of not more than 6 minutes and the replenishment rate of the water washing water and/or stabilizer is reduced to not more than 800 ml per square meter of photosensitive material.

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 color photographic photosensitive materials for camera use which comprises processing the material in a bath which has a bleaching function and which contains, as a bleaching agent, an aminopolycarboxylic acid ferric complex salt followed by a multi-stage counter-flow water washing and/or stabilization processing wherein the molecular weight of the aminopolycarboxylic acid of the aminopolycarboxylic acid ferric complex salt is from 300 to 450 and the water washing water and/or stabilizer is treated with a reverse osmosis membrane.

2. The method of processing a silver halide color photographic photosensitive material as in claim 1 wherein the bleaching agent is at least one bleaching agent selected from the group consisting of 1,3-diaminopropane tetraacetic acid ferric complex salt, 1,4-diaminobutane tetraacetic acid ferric complex salt, 1,5-diaminopentane tetraacetic acid ferric complex salt, trans-cyclohexanediamine tetraacetic acid ferric complex salt, glycol ether diamine tetraacetic acid ferric complex salt and diethylenetriamine pentaacetic acid ferric complex salt.

3. The method of processing a silver halide color photographic photosensitive material as in claim 1 wherein the processing time after processing in the bath has a bleaching function until reaching the drying process is 6 minutes or less.

4. The method of processing a silver halide color photographic photosensitive material as in claim 1 wherein the rate of replenishment of the water washing water and/or stabilizer which is subjected to reverse osmosis is 800 ml or less per square meter of photosensitive material.

5. The method of processing a silver halide color photographic photosensitive material as in claim 1, wherein the molecular weight is at least 300 to not more than 400.

6. The method of processing a silver halide color photographic photosensitive material as in claim 1, wherein the amount of the aminopolycarboxylic acid ferric complex salt is 0.1 to 1 mol/liter of the bleach bath or 0.05 to 0.5 mol/liter of the bleach-fix bath.

Fig. 1

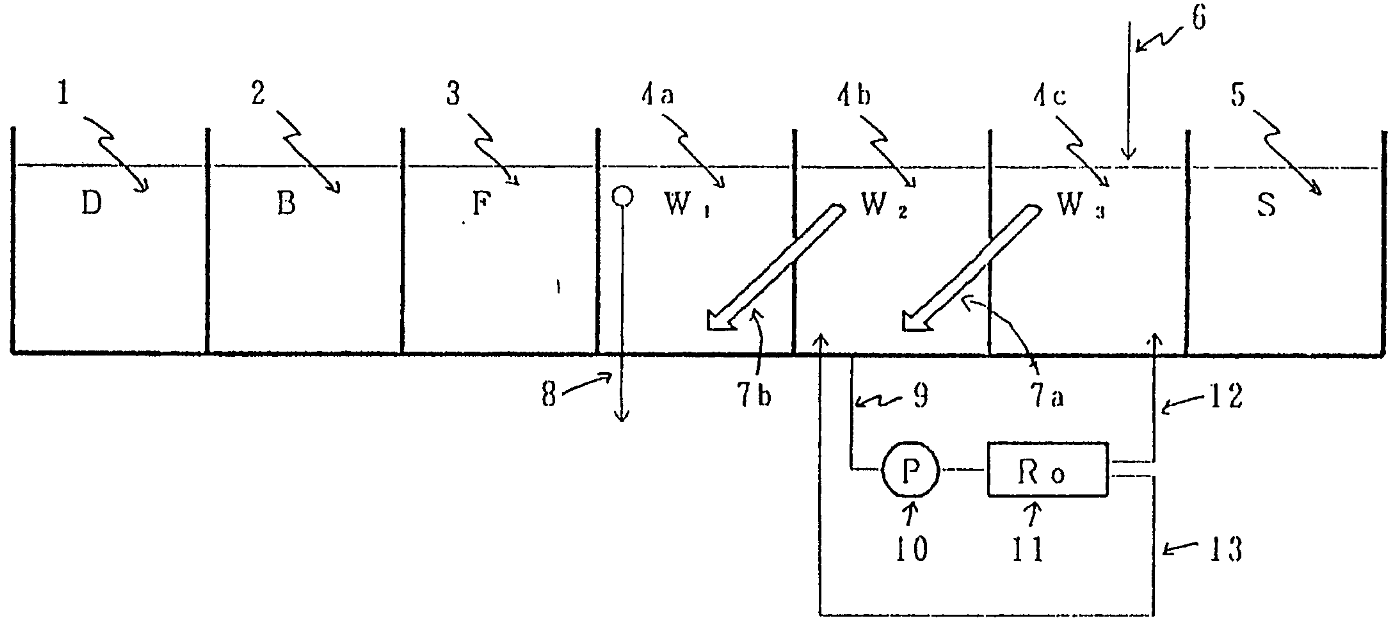


Fig. 2

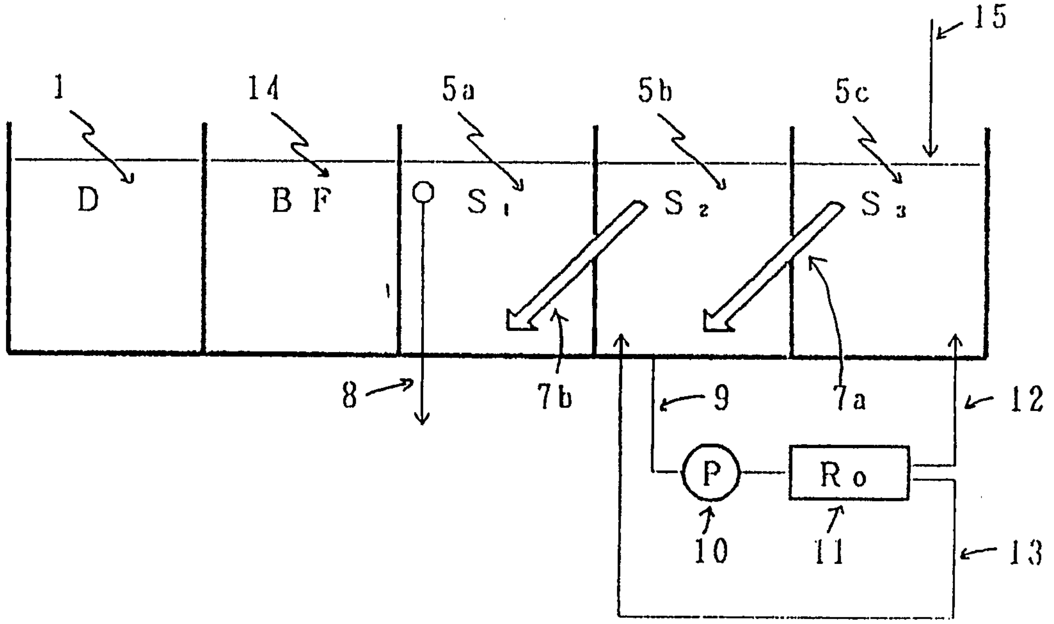


Fig. 3

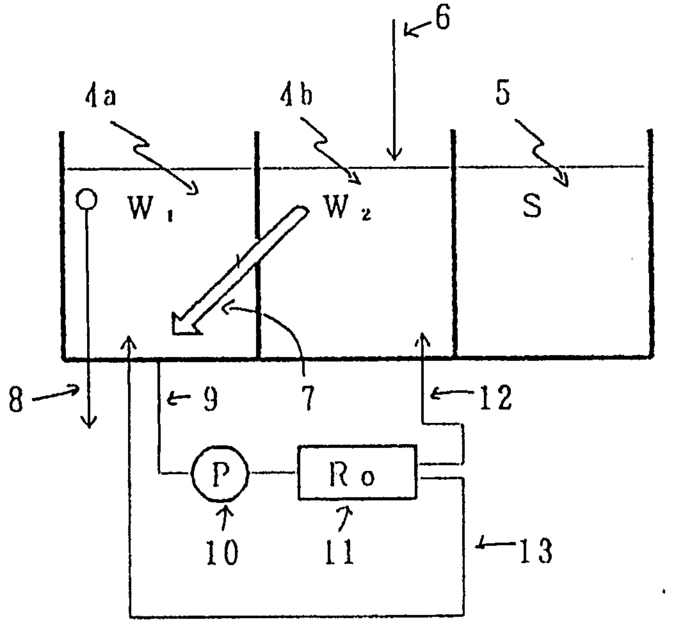
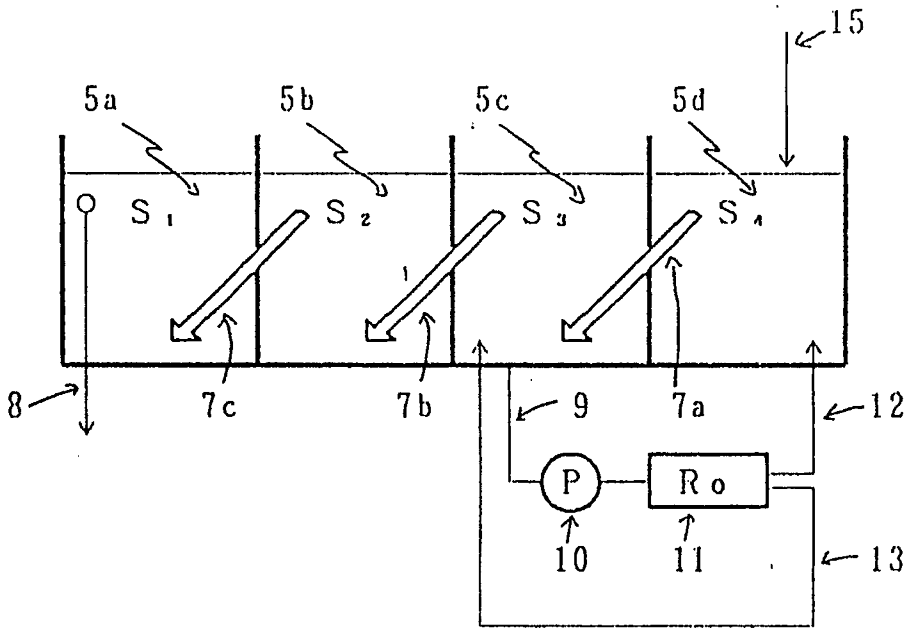


Fig. 4



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 12 5786

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	PATENT ABSTRACTS OF JAPAN vol. 10, no. 110 (P-450)(2167) 24 April 1986, & JP-A-60 241053 (KONISHIROKU PHOTO INDUSTRY CO LTD) 29 November 1985, * the whole document *	1-6	G 03 C 5/395 G 03 C 7/42
Y	EP-A-0 186 169 (KONISHIROKU PHOTO INDUSTRY CO LTD) * page 30, lines 16 - 27 * * page 35, line 31 - page 36, line 14 * * claim 4 * * figure 2 *	1-6	
Y	EP-A-0 329 052 (KONICA CORPORATION) * page 5, lines 4 - 8 * * page 44, lines 54 - 56 *	1-6	
Y	PATENT ABSTRACTS OF JAPAN vol. 13, no. 32 (P-817)(3380) 25 January 1989, & JP-A-63 231342 (FUJI PHOTO FILM CO.LTD.) 27 September 1988, * the whole document *	1-6	
Y	EP-A-0 147 148 (KONISHIROKU PHOTO INDUSTRY CO LTD) * page 11, lines 25 - 30 *	1-6	
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 133 (P-693)(2980) 22 April 1988, & JP-A-62 254151 (FUJI PHOTO FILM CO.LTD.) 05 November 1987, * the whole document *	1-6	
A	EP-A-0 224 858 (KONISHIROKU PHOTO INDUSTRY CO LTD) * claims 1, 2; figure 1 *	1-6	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	15 March 91	BOLGER W.

CATEGORY OF CITED DOCUMENTS

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

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

&: member of the same patent family, corresponding document