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[54] METHOD FOR RAPIDLY FORMING PHOTOGRAPHIC IMAGES

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** .... **96/50 R;** 96/63; 96/66 R; 96/67; 96/87 R; 96/95; 96/114

[51] **Int. Cl.²** ... **G03C 5/26;** G03C 5/24; G03C 1/72

[58] **Field of Search** .... 96/50, 63, 66, 66 T, 67, 96/87 R, 114, 95

[56] **References Cited**

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[57] ABSTRACT

A method for rapidly forming photographic images which comprises processing a photographic light sensitive material comprising at least one silver halide emulsion layer, and a gelatin derivative-containing upper most layer at a temperature of at least 30°C.

19 Claims, No Drawings

METHOD FOR RAPIDLY FORMING PHOTOGRAPHIC IMAGES

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The present invention relates to a method for rapidly forming photographic images and, more particularly, it is concerned with a novel method for rapidly forming photographic images with good quality using photographic processings at elevated temperatures.

2. DESCRIPTION OF THE PRIOR ART

In general, photographic light-sensitive materials contain a hydrophilic natural high molecular weight substance and/or a hydrophilic synthetic high molecular weight substance, as well as gelatin, in a silver halide emulsion layer, a photographic auxiliary layer such as an intermediate layer, a protective layer or an antihalation layer, or in a subbing layer interposed between these layers and a support. Photographic materials containing these hydrophilic high molecular substances are usually processed, after exposure, in various aqueous solutions which differ from each other in pH, salt concentration and solution temperature in the steps of development, stopping, fixing and washing (and bleaching in the case of color light-sensitive materials), in order to form photographic images.

However, where the processing temperature is high as in the case of rapid processing (i.e. the procedure of rapidly conducting development or other photographic processings to form images) of photographic light-sensitive materials or where the processing requires much time because of a number of steps for various purposes are involved as in the case of processing reversal color photographic materials, the photographic emulsion layers and other layers of the photographic light-sensitive materials become swollen and softened to too great a degree. This results in many disadvantages such as a reduction in the physical strength, the frequent formation of a network pattern called "reticulation", and an increase in the drying load after processing.

Removal of these disadvantages is preferable because they seriously reduce the commercial value of photographic light-sensitive materials regardless of whether the photographic materials are black-and-white light-sensitive materials or color light-sensitive materials.

In recent years, with the development of methods of processing photographic light-sensitive materials, it has been desired to conduct the photographic processing not at temperatures near room temperature of about 20°C or 24°C, but rather at elevated temperatures such as at 30°C, 38°C or 50°C, whereby each processing step can be shortened and the productivity in the photographic processing steps can be increased. Therefore, it is necessary to develop an image-forming technique using photographic light-sensitive materials which have excellent physical properties so that the above-described defects are not encountered even with rapid processing at an elevated temperature.

In the prior art relating to the satisfying of the above-described requirements, the previous incorporation in a photographic layer or a protective layer of a hardener (upon production of the photographic light-sensitive materials) in a very large amount e.g., on the order of several times or several 10 times as much as in the ordinary case, was considered so as to impart sufficient physical strength to resist severe processing conditions. However, although reticulation could be prevented to some extent, this method failed to prevent reticulation to a completely practical extent. In addition, in this method, the phenomenon in which the physical strength of the emulsion film undergoes a gradual change during storage of the photographic light-sensitive material, known as "post-hardening", tended to take place, which made the maintainance of photographic quality difficult. Furthermore, this method had the disadvantage that the degree of hardening of the photographic layers was increrased to such an extent that permeation and diffusion of a developer upon development processing was affected, which lead to a substantial reduction in sensitivity.

Other methods such as a method of processing an exposed photographic light-sensitive material in an aqueous solution bath, called a "pre-hardening bath", containing a hardener immediately before developing the material, a method of conducting development and hardening at the same time using a developer containing a hardener, and like methods are known.

However, these methods have the disadvantages that fog, deterioration of other photographic properties and, particularly with color light-sensitive materials, color stain, and similar unfavorable phenomena occur, such that the kind of appropriate light-sensitive materials and processing conditions as well as the kind of the hardener are narrowly limited, in order to obtain photographic layers possessing the necessary physical strength within a short period of time without deteriorating photographic properties. In practicular, because an additional pre-hardening bath step is contained in the former method, this method cannot be said to be an excellent method since the shortening of the photographic processing time and the simplification of the processing steps are not obtained.

Additional method for controlling reticulation include a method of coating carboxymethylated casein or ethyl cellulose sulfate sodium salt in advance on the uppermost layer of the emulsion side as a replacement for a gelatin protective layer usually employed in a photographic light-sensitive material. This method is believed to be advantageous in that the addition of a large amount of hardener to photographic layer is not required. However, carboxymethylated casein has the disadvantage that removal therefom of impurities which adversely affect the photographic properties is difficult. An additional production disadvantage is that it is difficult to form a uniform coating layer of this material on an emulsion layer due to the poor coating propety of an aqueous solution of carboxymethylated casein. Also, it is difficult to prepare an ethyl cellulose sulfate sodium salt having good solubility in water with good reproducibility. As can be surmized from the chemical structure of this sulfuric acid ester, the ester has a poor storage stability over a long period of time, lacks a setting property, and has poor coating property. Thus, these materials are not necessarily suitable in the production of photographic light-sensitive materials.

It is, therefore, an object of the present invention to provide a method for rapidly forming images with good quality by processing a silver halide photographic light-sensitive material at an elevated temperature.

Another object of the present invention is to provide an excellent photographic light-sensitive material in which softening or reticulation of the photographic layer does not take place during or after rapid processing at an elevated temperature.

A further object of the present invention is to provide a method for producing a photographic light-sensitive material having practical productivity, photographic properties and physical properties, and for conducting photographic processing thereof at a high temperature without deteriorating these characteristics, thus rapidly obtaining images with high quality.

SUMMARY OF THE INVENTION

As a result of extensive investigations, the inventors have found that the above-described objects can be attained by processing a silver halide photographic light-sensitive material containing at least one silver halide emulsion layer and containing a gelatin derivative-containing layer as an uppermost layer in photographic processing solutions maintained at a temperature of at least 30°C.

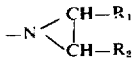
DETAILED DESCRIPTION OF THE INVENTION

The present invention provides the advantage that photographic images having excellent quality photographic and physical properties can rapidly be obtained. That is, the present invention provides the ability to reduce the change in the photographic and physical properties of the light-sensitive material before processing and to conduct rapid photographic processing without a deterioration in the photographic properties, such as fogging, reduction in sensitivity, etc., and without physical deterioration such as reticulation due to processing at an elevated temperature or over a wide pH range. A further advantage of the present invention is that, since the gelatin derivative incorporated in the uppermost layer provided on a photographic light-sensitive material has excellent solubility, excellent compatibility with other high molecular weight substances, excellent coating properties and the like, no difficulties in the production of photographic light-sensitive materials are encountered.

The gelatin derivative used in the present invention is a chemically modified gelatin which is produced as a result of processing gelatin with a monofunctional agent capable of reacting with an amino group, an imino group, a carboxyl group and/or a hydroxy group, contained in the polar or hydrophilic residue in the various amino acid fractions forming the gelatin molecules. The residue of the functional group containing agent suitably is present in an amount of from about 0.02 to about 1.5m mol/g, preferably from 0.05 to 1.0m mol/g in the gelatin derivative (on a dry basis).

The term "gelatin" which is used in the present specification as referring to the starting material of the gelatin derivative of the present invention, is also used to described the proteinic substance derived from collagen. Also, this term includes any other products which are substantially equivalent thereto, such as synthetic gelatins. Generally, as gelatin there are known the so-called "alkali-processed gelatin" derived from collagen through treatment with lime or the like, the so-called "acid-processed gelatin" with the processing being with hydrochloric acid or the like, the so-called "enzyme-processed gelatin" with the processing being with a hydrolase or the like, and low molecular weight gelatin obtained by further hydrolyzing the above-described gelatins using various methods. Any of these gelatins can be used for the production of the gelatin derivative necessary for practicing the present invention.

As the monofunctional reagents necessary for preparing the gelatin derivative to be used in the invention, any compound that possesses one functional group per molecule capable of reacting with an amino group, an imino group, a carboxyl group and/or a hydroxy group contained in the gelatin molecule can be used for preparing gelatin derivatives which are substantially equivalent in usefulness in the practice of the present invention. Representative functional groups are illustrated by the following: $-NCO$, $-NCS$, $-NHCOSO_3M$ or $-NHCS{\cdot}SO_3M$ (where M is an alkali metal such as sodium, potassium, etc.),



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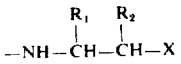
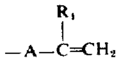


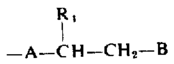
$$-NH-\overset{R_1}{\overset{|}{C}H}-\overset{R_2}{\overset{|}{C}H}-X$$

(where R_1 and R_2 each is a hydrogen atom or a lower alkyl group e.g., having up to 4 carbon atoms such as a methyl group or ethyl group; and X is a halogen atom such as Cl, Br, etc.),



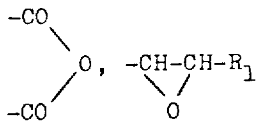
$$-A-\overset{R_1}{\overset{|}{C}}=CH_2$$

or

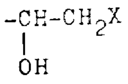


$$-A-\overset{R_1}{\overset{|}{C}H}-CH_2-B$$

(where R_1 is as defined above; A is an electron attracting group which activates a vinyl group (e.g., a halogen atom such as a chlorine atom or a bromine atom, an acetyloxy group, a sulfato group, etc.); B is an atom or atoms capable of forming a vinyl group upon elimination as an acid together with the hydrogen atom bonded to the adjacent carbon atom), $-So_2X$ (where X is as defined above), $-COX$ (where X is as defined above),

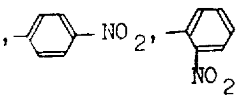


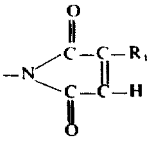
(where R_1 is as defined above),



$$-\underset{OH}{\underset{|}{C}H}-CH_2X$$

(where X is as defined above), $-X$ (where X is as defined above), $-COOR_3$(where R_3 is an aryl group having an electron attracting group at the o- or p-position

(e.g.,  , etc.)



(where R_1 is as defined above), and the like.

Representative examples of the agents having a functional group suitable for preparing the gelatin derivative used in the invention are illustrated below:

isocyanates such as phenyl isocyanate, p-tolyl isocyanate, 4-bromophenyl isocyanate, 4-chlorophenyl isocyanate, 2-nitrophenyl isocyanate, 4-ethoxycarbonylphenyl isocyanate, 1-naphthyl isocyanate, phenyl isocyanate·bisulfite adduct, p-biphenyl isocyanate·bisulfite adduct, etc. or a precursor thereof;

isothiocyanates such as phenyl isothiocyanate, p-tolyl isothiocyanate, phenyl isothiocyanate·bisulfide adduct, etc. or a precursor thereof;

aziridines such as N-pentanoyl-2-ethyl-1-aziridine, 1-phenylcarbamoylaziridine, 2-methyl-1-phenylcarbamoylaziridine, 1-dimethylaminosulfonylaziridine, 1-benzoylazridine, 4-nitrobenzyol-1-aziridine, 1-(2-chlorophenyl)carbamoyl-1-aziridine, 1-(3-methylphenyl)carbamoylaziridine, 1-(n-butylsulfonyl)aziridine, 1-(phenylsulfonyl-2-methylaziridine, 2-(1-aziridinyl)-4, 6-bisethylamino-1,3,5-triazine, 1-phenyl-3-(2-chloroethyl)urea, etc. or a precursor thereof;

activated vinyl compounds (e.g., containing groups such as a carbonyl group, a sulfonyl group, etc.) such as N-vinylsulfonyl-p-toluidine, vinylsulfonylbenzene, 1-methyl-4-vinylsulfonylbenzene, acrylonitrile, 1-(hydroxysulfonyloxy)-2-(4-methoxyphenylsulfonyl)ethane, 2-phenylcarbamoylethyl bromide, etc. or a precursor thereof;

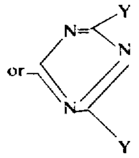
sulfonyl halides such as, the arylsulfonyl halides, e.g., benzenesulfonyl chloride, 4-methoxybenzenesulfonyl chloride, 4-phenoxybenzenesulfonyl chloride, 4-chlorobenzenesulfonyl chloride, 4-bromobenzenesulfonyl chloride, 4-methylbenzenesulfonyl chloride, 3-nitrobenzenesulfonyl chloride, 3-carboxybenzenesulfonyl chloride, 2-naphthalenesulfonyl chloride, 4-aminobenzenesulfonyl fluoride, 3,4-diaminobenzenesulfonyl fluoride, 3-carboxybenzenesulfonyl fluoride, etc. and the lower alkylsulfonyl halides such as methanesulfonyl chloride and ethansulfonyl chloride, etc.;

carboxylic acid halides such as the arylcarboxylic acid halides, e.g., 4-nitrobenzoyl chloride, 4-carboxybenzoyl bromide, etc.; and the aliphatic carboxylic acid halides, e.g., butyric acid chloride, caproic acid chloride and caprylic acid chloride, etc,;

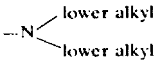
carboxylic acid anhydrides including aromatic and aliphatic carboxylic acid anhydrides such as succinic anhydride, phthalic anhydride, hexahydrophthalic anhydride, isatoic acid anhydride, monomethylsuccinic acid anhydride, glutaric acid anhydride, benzoic acid anhydride, trimellitic acid anhydride, 3,6-dichlorophthalic acid anhydride, diglycollic acid anhydride, nitrophthalic acid anhydride, etc.;

oxirane ring-containing compounds such as 3-phenyloxy-1,2-epoxypropane, 3-(3-methylphenyloxy)-1,2,-epoxypropane, 3-(2,4-dibromophenyloxy)-1,2-epoxypropane, 3-(4-acetylaminophenyloxy)-1, 2-epoxypropane, 3-(2-biphenyloxy)-1,2-epoxypropane, 3-(2,4-dinitro-1-naphthoxy)-1,2-epoxypropane, 1-chloro-2-hydroxy-3-phenyloxypropane, epichlorohydrin, 1-bromo-2-hydroxy-3-(2-chlorophenyl)propane, etc. or a precursor thereof;

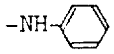
active halogen containing compounds as described by, for example, the following formula: D-X {wherein X is a halogen atom; D is a residue which is capable of activating X; e.g., $—CH_2COOH$



(where Y is a lower alkyloxy group; an aryloxy group such as phenoxy; an —NH— lower alkyl group; and



or an —NH-aryl group such as



} such as bromoacetic acid, chloroacetic acid, 2-chloro-4,6-dimethoxy-1,3,5-triazine and 2-chloro-4,6-diethylamino-1,3,5-triazine, etc.;

activated esters of carboxylic acids including aromatic acid and aliphatic acids such as o-nitrophenyl benzoate, p-nitrophenyl acetate, p-nitrophenyl-1-hydroxynaphthoate, etc.; and

maleimides such as N-ethylmaleimide, N-phenylmaleimide, N-(p-carboxyphenyl)-maleimide, N-(p-sulfophenyl)maleimide, N-(carboxymethyl)-maleimide, etc.

These reagents can be used to chemically modify gelatin employing the method to be described hereinafter, and the resulting gelatin derivatives, as the material used in the uppermost layer of the photographic light-sensitive material of the present invention, influence greatly the ability of the photographic light-sensitive of the present invention to the aforesaid aptitude for rapid processing at an elevated temperature. Of the above-illustrated reagents, isocyanates such as phenyl isocyanate, p-tolyl isocyanate, etc., aziridines such as 1-phenylcarbamoylaziridine, 2-methyl-1-phenylcarbamoylaziridine, 1-dimethylaminosulfonylaziridine, 1-benzoylaziridine, etc., and sulfonyl halides such as benzenesulfonyl chloride, 4-methoxybenzenesulfonyl chloride, 4-chlorobenzenesulfonyl chloride, 4-bromobenzenesulfonyl chloride, 4-methylbenzenesulfonyl chloride, etc. are particularly preferred reagents, either because they are economically advantageous due to their availability, or because they have a marked effect in preventing reticulation in processing at higher temperatures, for example, 48°C or 52°C.

The gelatin derivatives necessary for practicing the present invention can be prepared using a conventional technique by reacting gelatin with the above-described monofunctional reagent (compound having one functional group per molecule capable of reacting with the reactive group in the gelatin molecule) in a solvent for gelatin such as water, an organic solvent (e.g., dimethylsulfoxide, dimethylformamide, acetic acid, etc.) or a mixture of an organic solvent and water, in the presence of, if necessary, a base or an acid as a pH-adjusting agent. The above-described process for preparing the gelatin derivatives used in the present invention is the same as or similar to known processes and described in, e.g., U.S. Pat. Nos. 2,594,293, 2,614,929, 2,763,639, 3,118,766, 3,132,945, 3,186,846, British Pat. Nos. 648,926, 976,391 and Japanese Patent Publication No. 26845/67.

However, the present invention is clearly distinguished from the above-described known patents. According to the descriptions in the above-described patents, all of the objects and the effects thereof relate to processes for the production of gelatin derivatives or to processes for the production of precipitated silver halide emulsions. Therefore, the present invention which relates to the method of incorporating gelatin derivatives prepared by treating gelatin with the foregoing monofunctional reagents, in the uppermost layer of a photographic light-sensitive material for the purpose of producing photographic light-sensitive materials having good characteristics for rapid processing at an elevated temperature, is completely different from the above recited prior art.

In the present invention, the gelatin derivative is not necessarily incorporated in the photographic emulsion layer of a photographic light-sensitive material to be processed at a high temperature. All that is required is that the gelatin derivative be incorporated in the protective layer on an emulsion layer or to provide a layer comprising the gelatin derivative alone as the protective layer on the emulsion layer. In this case, two or more gelatin derivatives can be used in combination. Also, a photographic light-sensitive material used in the invention having good characteristics for rapid processing at an elevated temperature can be obtained by incorporating the gelatin derivative in the uppermost layer provided on a photographic light-sensitive material having a conventional protective layer, or by providing a layer comprising the gelatin derivative alone as an uppermost layer on the conventional protective layer.

As described above, the uppermost layer provided on a photographic light-sensitive material used in the present invention can comprise either the gelatin derivative alone or a mixture of the gelatin derivative and another hydrophilic binders. As the other hydrophilic binder, all known binders or analogous binders can be employed. In particular, natural high molecular weight substances such as non-modified gelatin, albumin, casein, agar-agar, sodium alginate, water-soluble starch, etc.; cellulose derivatives such as carboxy cellulose alkyl (e.g., methyl) esters, hydroxyethyl cellulose, carboxymethyl hydroxyethyl cellulose, etc.; and synthetic polymers such as polyvinyl alcohol, partially esterified polyvinyl alcohol, polyacrylamide or derivatives thereof, polyvinylpyrrolidone, polyacrylic acid or polyacrylate, or various copolymer thereof, and various copolymers of maleic anhydride and another vinyl compound; etc., are preferable. The ratio of the gelatin derivative to these hydrophilic binders is not particularly limited and can vary; but, in order to markedly promote the effect obtained by the practice of the present invention, the gelatin derivative content is preferably not than 20%, based on the weight of total binders forming the uppermost layer.

As the developer employable in the photographic processing in the present invention, any developer capable of reducing silver halide to silver can be used.

In the case of black-and-white development, developers containing as the developing agent polyhydroxybenzenes, 4-aminophenols, 3-pyrazolidones, p-phenylenediamines, ascorbic acid, N-(p-hydroxy phenyl)glycine, other developing agents as disclosed in C.E.K. Mees & T.H. James *The Theory of Photographic Process*, Third Edition (1966) MacMillan Co., Chapter 13 and L.F.A. Mason *Photographic Processing Chemistry* (Oxford Press 1966) pp 16–30, or a mixture thereof can be used. Suitable polyhydroxy benezenes include, e.g., hydroquinone, 2-methylhydroquinone, 2-phenylhydroquinone, 2-chlorohydroquinone, pyrogallol, catechol, etc. Suitable 4-aminophenol include, e.g., 4-N-methyl-aminophenol hemisulfate (conventionally called "Metol"), 4-N-benzyl-aminophenol chloride, 4-N,N-diethylaminophenol chloride, 4-aminophenol sulfate, etc. Suitable 3-pyrazolidones include, e.g., 1-phenyl 3-pyrazolidone, 4,4-dimethyl-1-phenyl-3-pyrazolidone, 4-methyl-1-phenyl-3-pyrazolidone, etc.

In the case of color development, developers containing as the developing agent an aromatic primary amines such as p-phenylenediamine, for example, inorganic acid salts of 4-amino-N,N-diethylaniline; 2-amino-5-diethylaminotoluene; 2-amino-5-(N-ethyl-N-laurylamino)toluene; 4-[N-ethyl-N-(β-hydroxyethyl)-amino] aniline; 3-methyl-4-amino-N-ethyl-N-(β-hydroxyethyl)aniline; 4-amino-3-methyl-N,N-diethylaniline; 4-amino-3-methyl-N-ethyl-N-(2-methanesulfonylaminoethyl)aniline as disclosed in U.S. Pat. No. 2,193,015; N-(2-amino-5-diethylaminophenylethyl) methanesulfoamide, N,N-dimethyl-p-phenylenediamine as disclosed in U.S. Pat. No. 2,592,364; 3-methyl-4-amino-N-ethyl-N-methoxyethylaniline as disclosed in Japanese Patent laid open to inspection No. 64933/73, or the like can be used. More detailed materials on color developing agents are described in L.F.A. Mason *Photographic Processing Chemistry* Focal Press-London (1966) pp226–229. 3-pyrazolidones in combination with the color developing agent also can be used.

In order to further promote the effects of the present invention, a hardener, a matting agent, a lubricant or the like can be used in suitable amounts in combination with the gelatin derivative incorporated in the uppermost layer. It is well known, as a means necessary for promoting the effect of the protective layer, to add the above-described gelatin additives to the protective layer of conventional photographic light-sensitive materials. In the present invention it is preferable to use them for the same purpose also. That is, a hardener is effective to suitably harden the uppermost layer to maintain the physical strength of the surface layer. Particularly preferred examples of hardeners are: aldehyde series compounds such as formaldehyde, glutaraldehyde and halocarboxyaldehydes (e.g. mucochloric acid); ketones such as diacetyl and cyclopentanedione; active halogen-containing compounds such as bis(2-chloethyl urea), 2-hydroxy-4,6-dichloro-1,3,5-triazine and those compounds as disclosed in U.S. Pat. Nos. 3,288,775 and 2,732,303 and British Pat. Nos. 974,723 and 1,167,207; active olefin-containing compounds such as divinylsulfone, 5-acetyl-1,3-diacryloylhexahydro-1,3,5-triazine and those compounds as disclosed in U.S. Pat. Nos. 3,635,718; 3,232,763; 3,490,911 and 3,642,486 and British Pat. No. 994,869; N-methylol compounds such as N-hydroxymethylphthalimide and those compounds as disclosed in U.S. Pat. Nos.

2,732,316 and 2,586,168; isocyanates as disclosed in U.S. Pat. Nos. 3,103,437; aziridines as disclosed in U.S. Pat. Nos. 3,017,280 and 2,983,611; acid derivatives as disclosed in U.S. Pat. Nos. 2,725,294 and 2,725,295; carbodiimide series compounds as disclosed in U.S. Pat. Nos. 3,100,704; epoxy compounds as disclosed in U.S. Pat. No. 3,091,537; isooxazol series compounds as disclosed in U.S. Pat. Nos. 3,321,313 and 3,543,292; dioxane derivatives such as dihydroxydioxane and dichlorodioxane and inorganic hardeners such as chrom alum and zirconium sulfate, precursors of the above-described materials such as addition compounds of an alkali metal bisulfite and an aldehyde, methylol derivaties of hydrazine, and primary aliphatic nitro alcohols and those compounds as disclosed in U.S. Pat. Nos. 3,288,775; 3,017,280 and 2,983,611 and British Pat. No. 1,167,207. A matting agent is useful for preventing inconvenient adhesion difficulties between the uppermost layer and the surface of other substances. As the matting agent, there are preferably used silver halide grains of a suitable grain size; inorganic compounds such as silica, strontium barium sulfate, etc.; water-dispersable vinyl polymers such as polymethyl methacrylate, etc. A lubricant is useful for preventing adhesion difficulties similar to the matting agent and, in addition, is effective for improving friction properties which relates to the camera adaptation of movie films upon photographing or projection. Specifically, waxes such as liquid paraffin, higher fatty acid esters, etc.; polyfluorinated hydrocarbons or derivatives thereof; silicones such as polyalkylpolysiloxane, polyarylpolysiloxane, polyalkylpolysiloxane or the alkylene oxide adduct derivaties thereof; and the like are preferably used. These materials are each used for their known purposes and are used suitably in an amount effective to achieve the purpose of their use. An effective amount of the materials can each range from 0.01 to 90% wt., preferably from 0.05 to 50 wt% on a solids basis of the uppermost layer.

If necessary, a coating acid can be used for coating the uppermost layer for the same reasons such is used in coating other hydrophilic colloidal layers constituting a photographic light-sensitive material. Any of the known surface active agents can be employed and specifically, anionic surface active agents containing acidic groups such as a carboxylic acid group, a sulfonic acid group, a phosphoric acid group, a sulfate group, a phosphate group, etc., ampholytic surface active agents of carboxylic acid type, sulfonic acid type, sulfate type or phosphate type; nonionic surface active agents of the polyalkyleneoxide series or the polyglycerin series; and natural surface active agents such as saponin, are preferably used. Suitable such materials and the amounts thereof generally suitable for use are disclosed for example, in U.S. Pat. Nos. 2,600,831; 3,068,101; 3,415,649; 3,617,286; 2,271,623; 2,240,472; 2,288,226; 2,739,891; 3,158,484; 3,201,253; 3,210,191; 3,294,540; 3,415,649; 3,441,413, 3,442,654; 3,475,174; 3,545,974; German OLS No. 1,942,665; and British Pat. Nos. 1077317, and 1198450.

When the present invention is practiced in this manner, a positive light-sensitive material for movie use, which conventionally has been photographically processed at a temperature as low as 24°C for a comparactively long period of time, can be processed at an elevated temperature of, for example, 52°C in a short time to thereby form images of high quality.

A temperature preferably not higher than about 60°C can be employed. While it is necessary in the method of the present invention to develop the photographic light-sensitive material at a temperature of at least 30°C., processings other than development can be practiced at a temperature of some what lower than 30°C.

Also, the present invention is markedly effective where it is intended to improve the processing steps of reversal color light-sensitive materials by shortening the processing time. Such steps involve black-and-white development and color development and, therefore, take a long time in comparison with other light-sensitive materials. That is, the present invention enables reversal color light-sensitive materials to be processed without reticulation resulting when the temperature of the processing steps is changed completely or partially from a low temperature of 24°C or 29°C to a high temperature of, for example, 38°C or 46°C and, therefore, enables images to be formed with excellent quality in a short time. In addition, the present invention enables first development, color development, bleach-fixation and like processing to be conducted immediately after photographing, without the necessity for a pre-hardening bath treatment which has conventionally been inevitable with reversal color photographic light-sensitive materials. Thus, the present invention provides the advantage that the processing time can be shortened and the processing steps can be reduced in the number of baths required without delaying the developing speed (or reduction in sensitivity) which has been encountered in the case of an exceptional hardening of the photographic layers so as to prevent reticulation.

The detailed mechanism on how reticulation in high temperature-processing can markedly be controlled by providing an uppermost layer comprising or containing the gelatin derivative on a photographic layer coated on a support is not yet completely clear. However, based on assumptions made from the experimental results obtained and while not desiring to be bound one factor could be that the swelling behavior, upon photographic processing, of the hydrophilic binder-containing photographic layer provided on a support favorably changes so as to prevent reticulation due to the influence of the gelatin derivative-containing uppermost layer. That is, it is believed that when a silver halide photographic light-sensitive material with the uppermost layer of the gelatin derivative used in the present invention is photographically processed at temperatures of 30°C or above, the swelling of the photographic emulsion layer in the direction parallel to the support is restricted as compared with swelling in the vertical direction to the support, thereby contributing to the prevention of reticulation.

It is known that the reticulation, which occurs when a gelatin layer provided in a support is swollen with water, becomes conspicuous when the swelling in the lateral direction along the support becomes great (see *Photographic Gelatin*, p.60, R.J. Cox, Ed., Academic Press, London (1972)). However, it was found that, when a silver halide photographic light-sensitive material having an uppermost layer containing the gelatin derivative of the present invention is photographically processed at temperatures not at 30°C or above, even though swelling in the vertical direction is very great, swelling in the lateral direction is controlled. This was a completely unexpected and surprising discovery.

The gelatin derivative used in the invention can be used as the subbing layer between the support and the photographic emulsion layer, or as the binder for an intermediate layer, a filter layer, a stripping layer or a backing layer, as well as the element for the uppermost layer or for the protective layer.

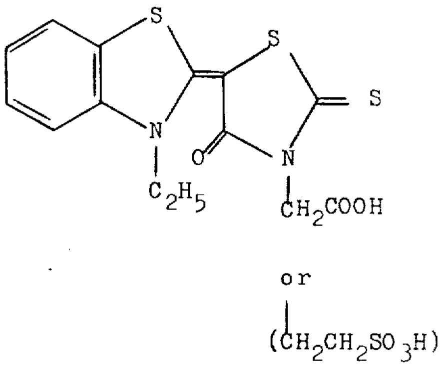
In practicing the present invention, the photographic layers having the gelatin derivative-containing uppermost layer thereon can include a photographic emulsion layer wherein various silver salts such as silver chloride, silver bromide, silver iodide, and mixed silver halides (e.g., silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc.) are used. Illustrative of such emulsions are various silver halide photographic emulsions such as orthochromatic emulsions, panchromatic emulsions, emulsions for infrared rays, emulsions for recording invisible light such as X-rays, color photographic emulsions (e.g., emulsions containing a color former, emulsions containing a dye developing agent, emulsions containing a bleachable dye, etc.). As the dispersing medium (or binder) for these photographic emulsions, gelatin, colloidal albumin, various gelatin derivatives (e.g., phthaloylated gelatin, malonoylated gelatin, etc.), cellulose derivatives (e.g., cellulose sulfate, hydroxyethyl cellulose, etc.), synthetic high polymers such as polyvinyl compounds (e.g., polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylamide, polystyrenesulfonic acid, etc.), gelatin-synthetic high polymer mixtures, and the like can be used. In addition, as the support for the photographic light-sensitive materials used in the present invention, various photographic supports such as a cellulose ester film, a polyvinyl acetate film, a polyethylene terephthalate film, a polystyrene film, relating films, paper, polyethylene-coated paper, synthetic paper, and the like are preferably used.

The silver halide photographic emulsion used in the present invention can be chemically sensitized in a conventional manner. Examples of suitable chemical sensitizers are active gelatin, gold compounds such as chloroanrate and gold chloride as disclosed in U.S. Pat. Nos. 2,399,083, 2,540,085, 2,597,856 and 2,597,915; salts of noble metals such as platinum, paladium, iridium, rhodium and ruthenium as disclosed in U.S. Pat. Nos. 2,448,060; 2,540,086; 2,566,245; 2,566,263 and 2,598,079; sulfur compounds which are capable of reacting with silver halide to produce silver sulfide as disclosed in U.S. Pat. Nos. 1,574,944; 2,410,689; 3,189,458 and 3,501,313; reducing materials such as stannous salts and amines as disclosed in U.S. Pat. Nos. 2,487,850; 2,518,698; 2,521,928; 2,521,926; 2,694,637; 2,983,610 and 3,201,254.

The silver halide photographic emulsion used can be spectrally sensitized or supersensitized with at least one of the polymethinedyes such as the cyanine dyes including the merocryanine dyes and the like, optionally in combination with a styryl dyestuff or a substantially colorless aromatic compound. Examples of blue-sensitizing dyes are those as disclosed in U.S. Pat. Nos. 2,493,748; 2,519,001; 2,977,229; 3,480,434; 3,672,897 and 3,703,377. Examples of green-sensitizing dyes are those as disclosed in U.S. Pat. Nos. 2,688,545; 2,912,329; 3,397,060; 3,615,635 and 3,628,964; British Pat. Nos. 1,195,302; 1,242,588 and 1,293,862; German OLS Nos. 2,030,326 and 2,121,780 and Japanese Patent Publication Nos. 4936/'68 and 14030/'69. Examples of red-sensitizing dyes are those as disclosed in U.S. Pat. Nos. 3,511,664; 3,522,052; 3,527,641; 3,615,613; 3,615,632; 3,617,295; 3,635,721 and 3,694,217 and British Pat. Nos. 1,137,580 and 1,216,203. Suitable examples of sensitizing dyes disclosed in the above cited references are shown below:

Sensitizing Dyes for the Blue-Sensitive Layer:

(I)



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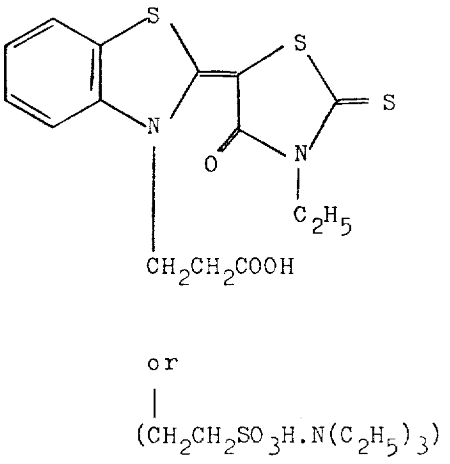

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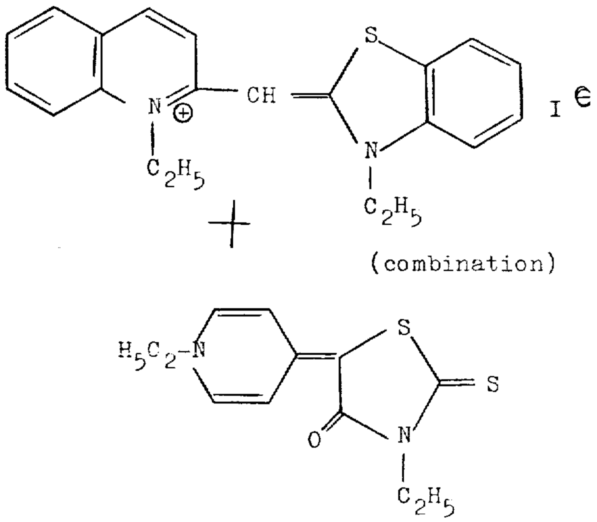

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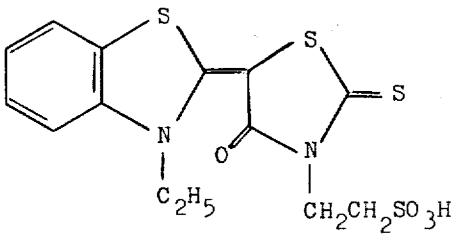
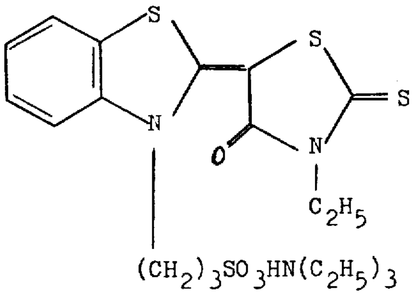


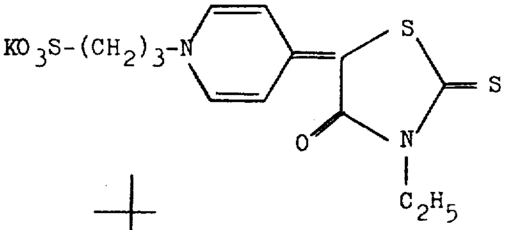
with yellow coupler
(combination)

(V)



with yellow coupler
(combination)

(VI)



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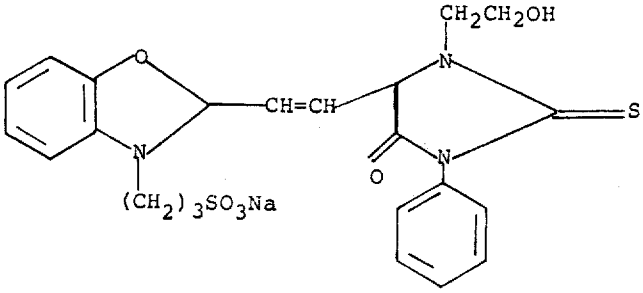
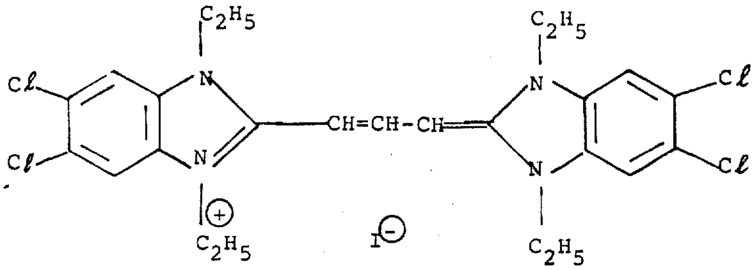


Sensitizing Dyes for the Green-sensitive Layer;

(VII)



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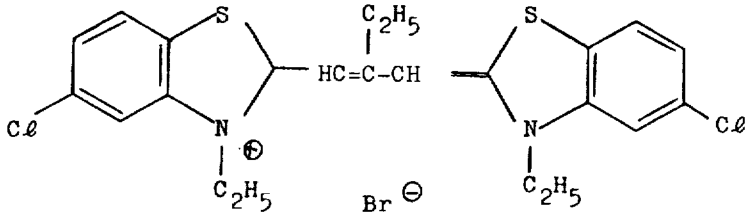

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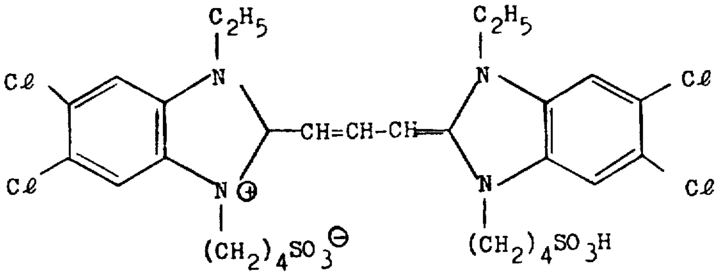

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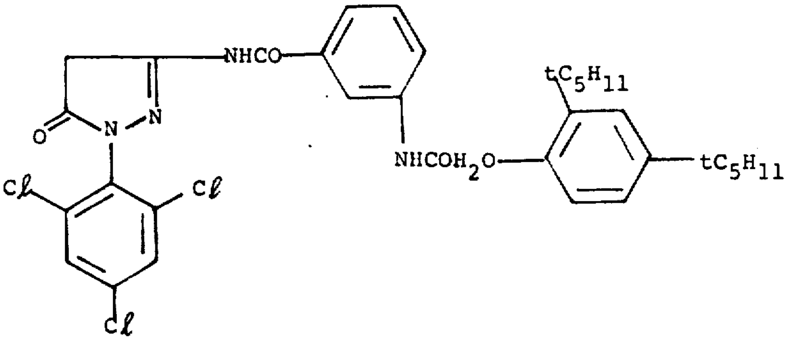

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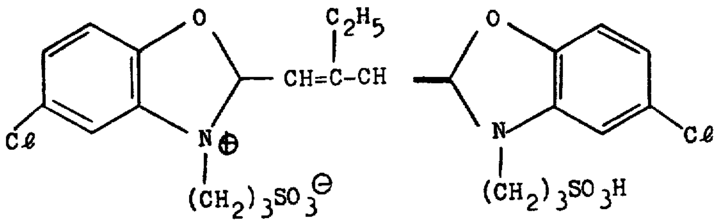

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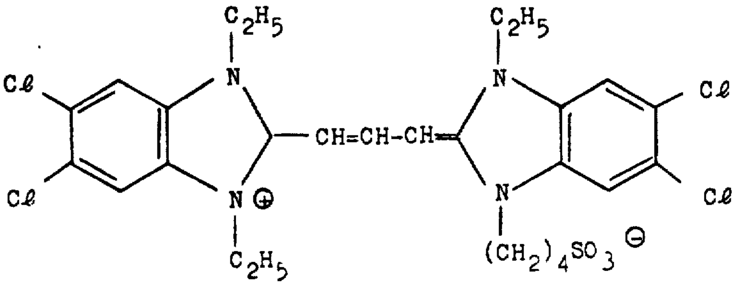

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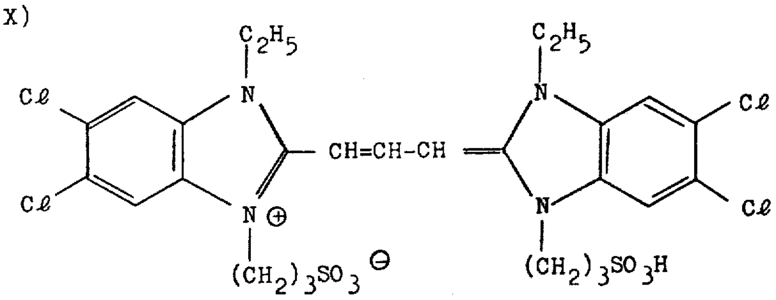

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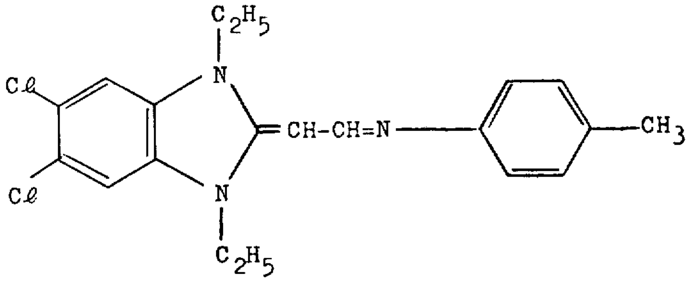

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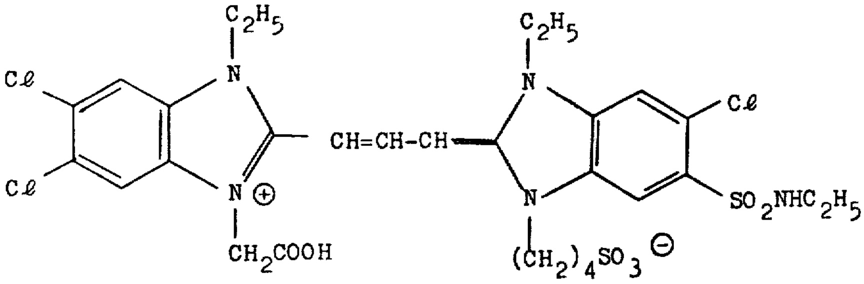

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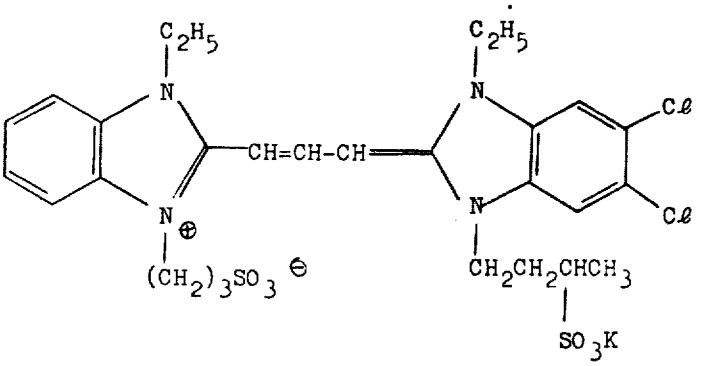

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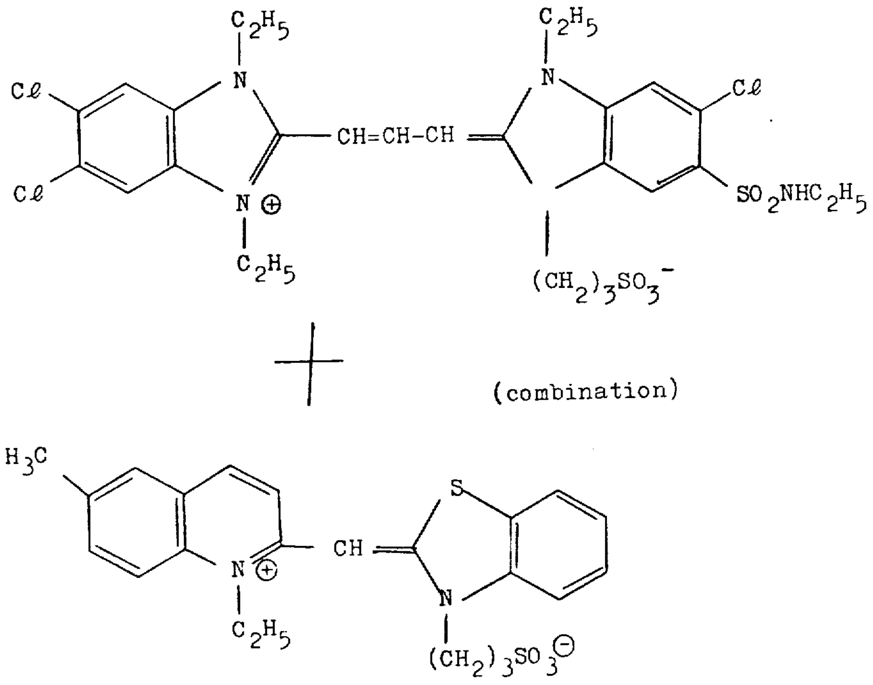

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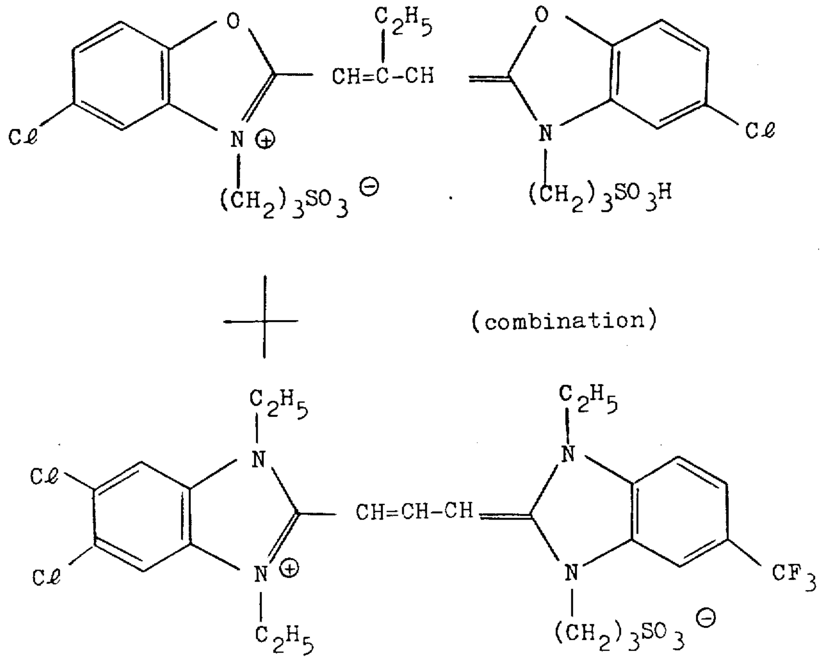

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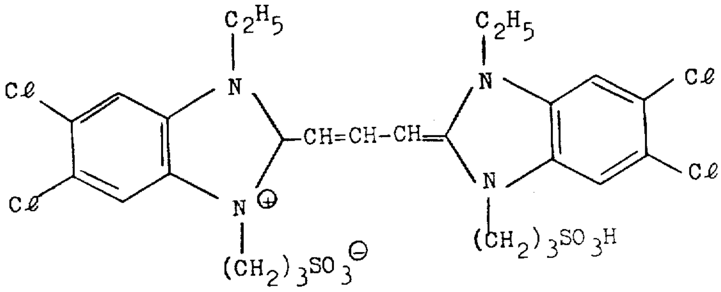

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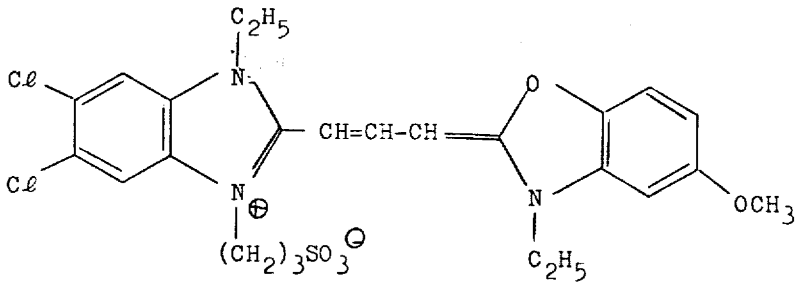

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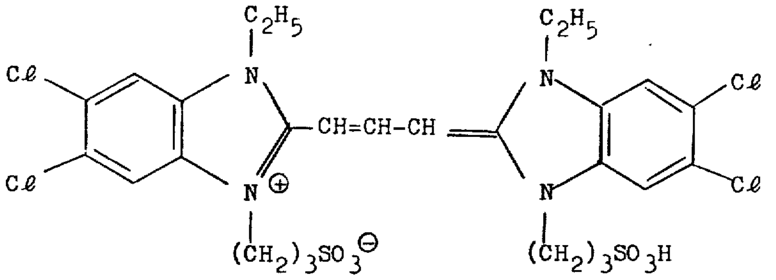

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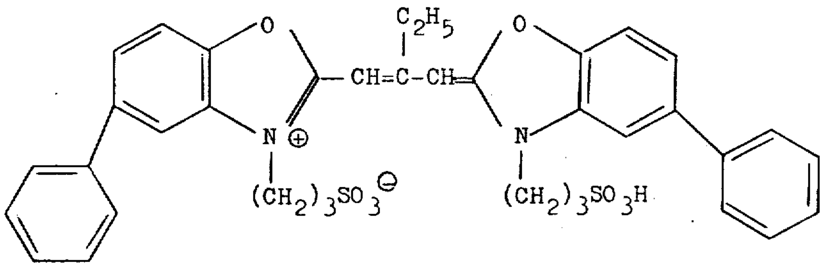

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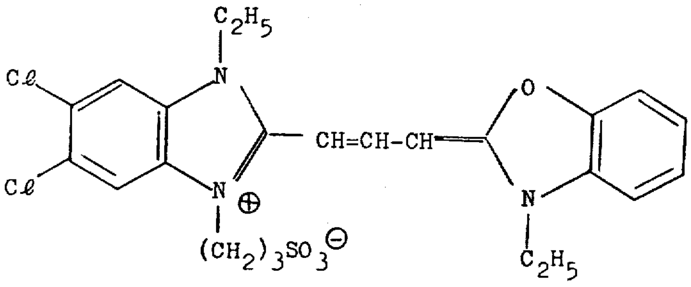
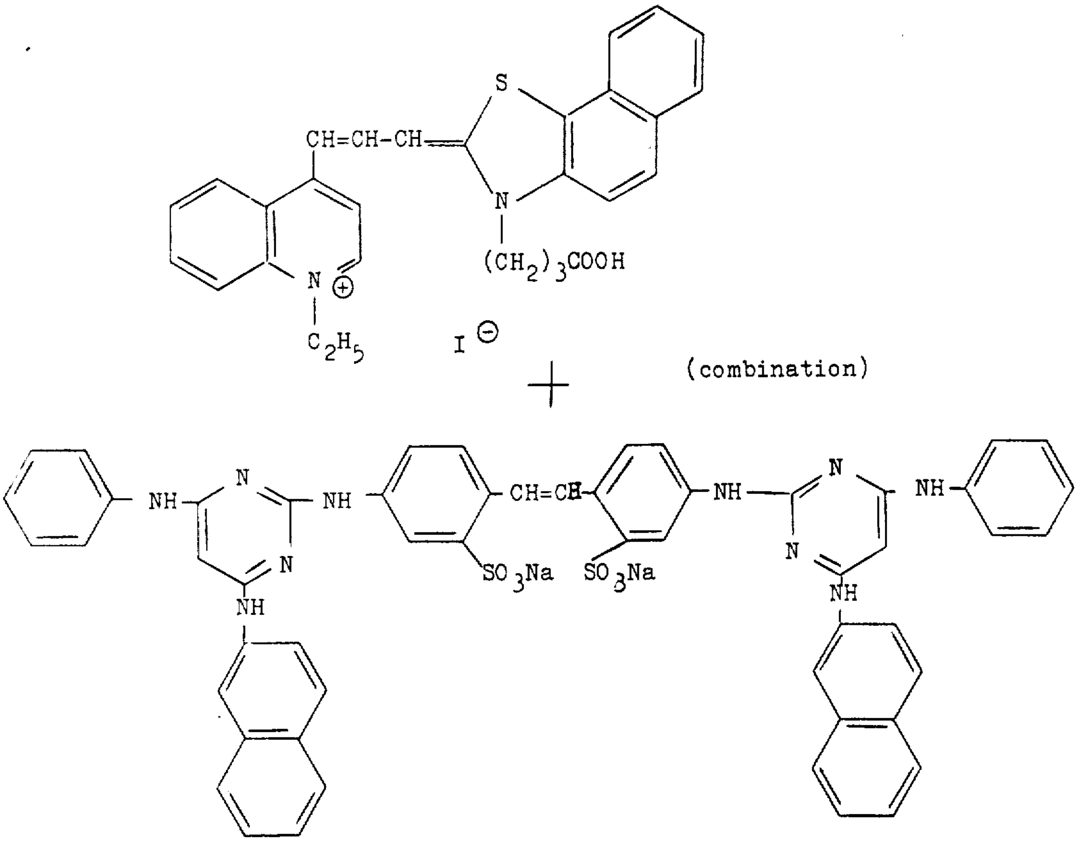


Sensitizing Dyes for the Red-Sensitive Layer:

(XVIII)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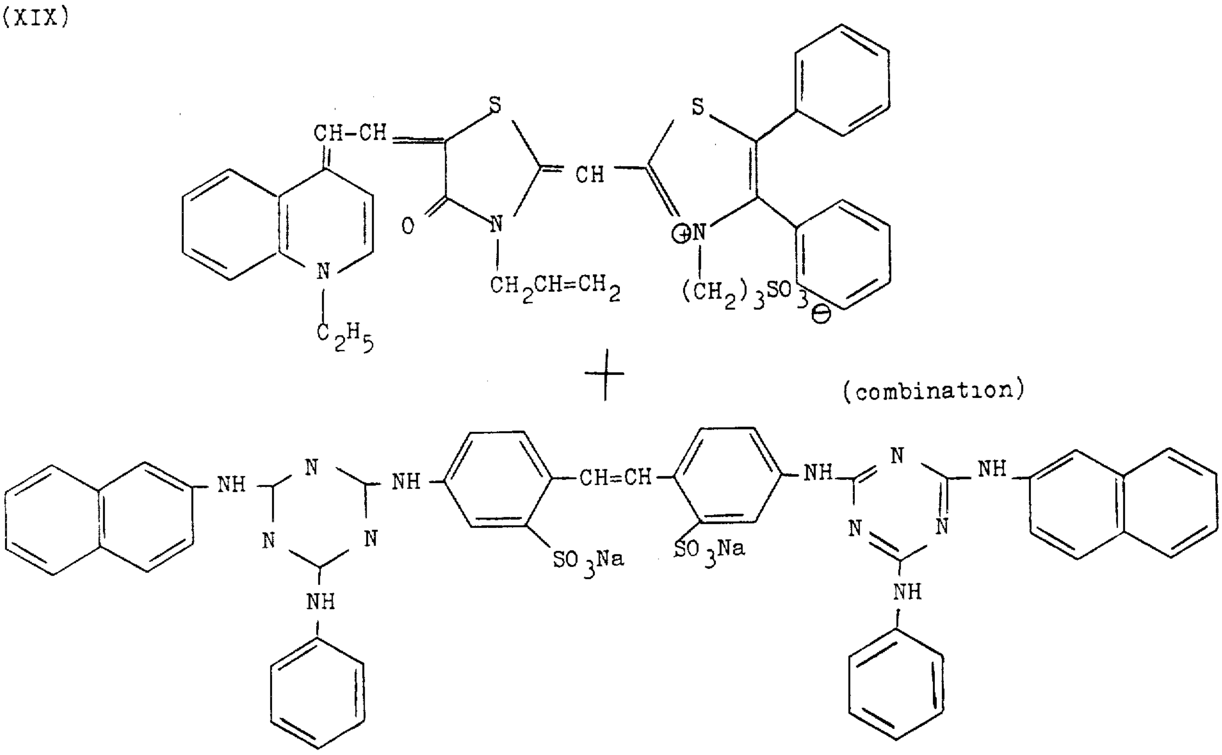
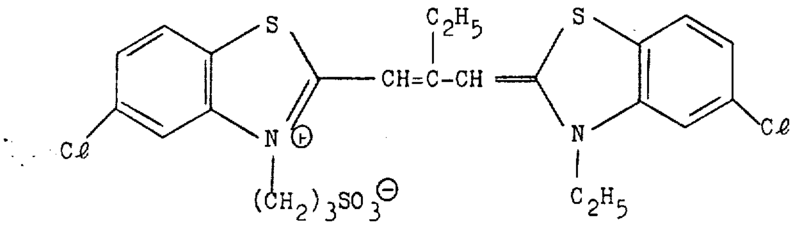
CH=CH-CH
N
$(CH_2)_3COOH$
N ⊕
C_2H_5
I ⊖
(combination)
NH
N
NH
N
NH
CH=CH
SO_3Na
SO_3Na
NH
N
N
NH
NH

(XIX)


CH-CH
S
S
CH
O
N
$CH_2CH=CH_2$
⊕N
$(CH_2)_3SO_3$ ⊖
N
C_2H_5
(combination)
NH
N
NH
N
N
NH
CH=CH
SO_3Na
SO_3Na
NH
N
NH
N
N
NH

(XX)



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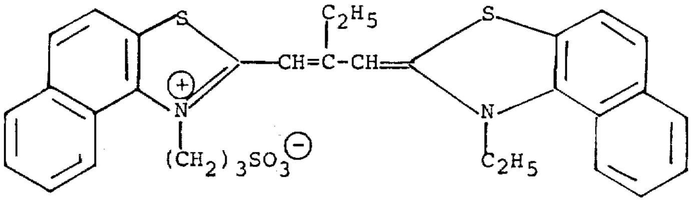

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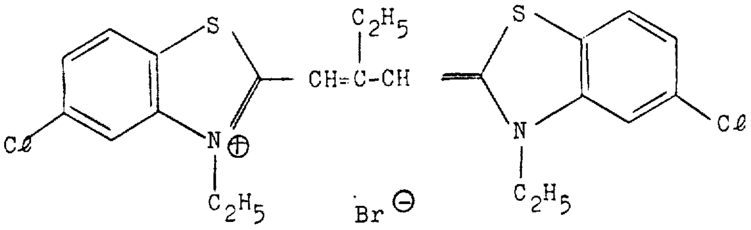

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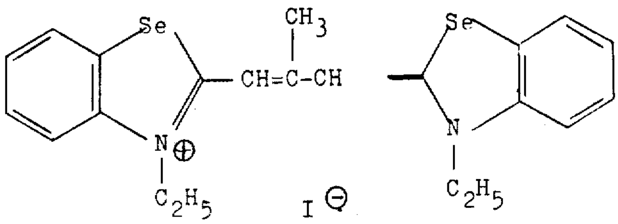

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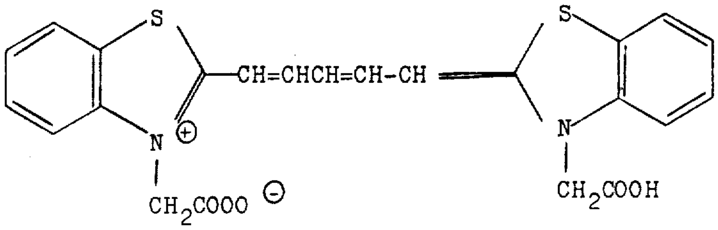

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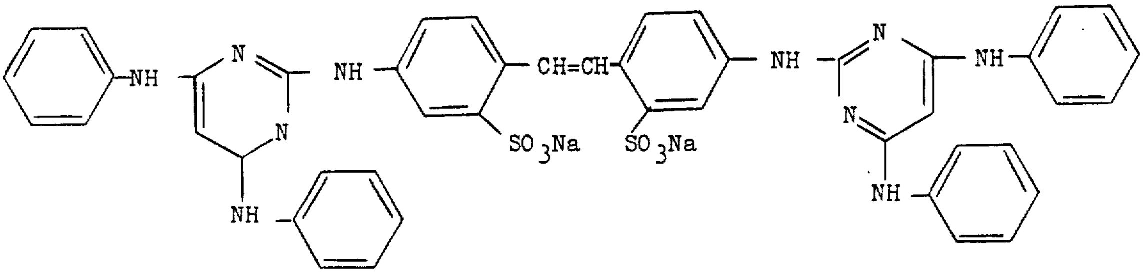

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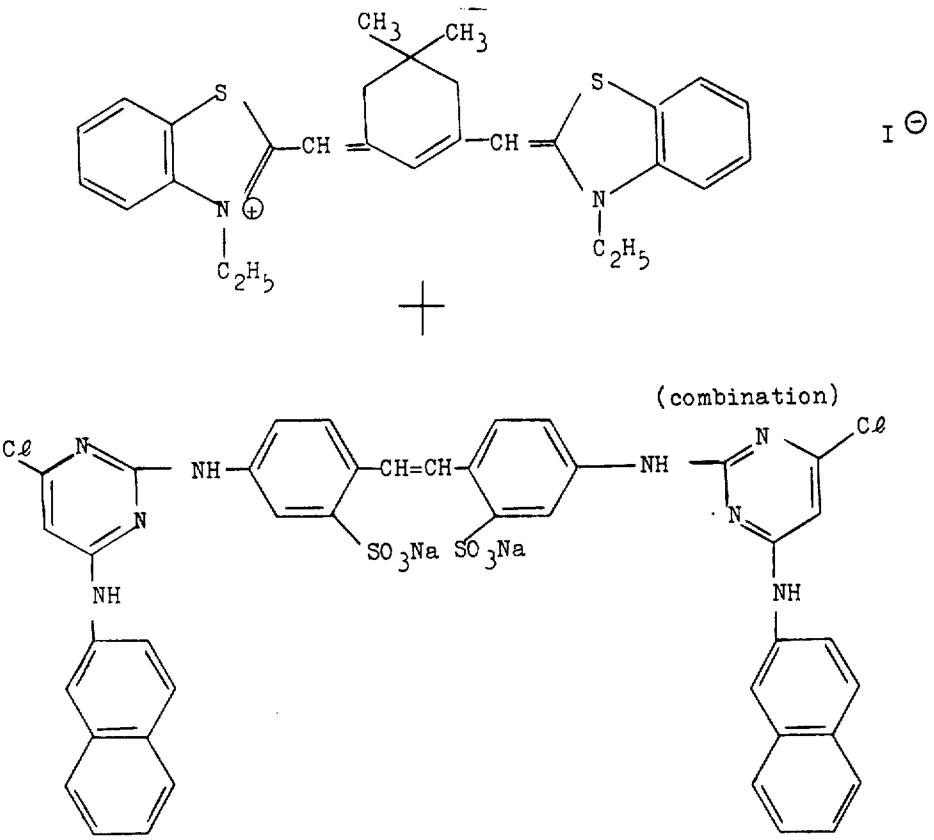

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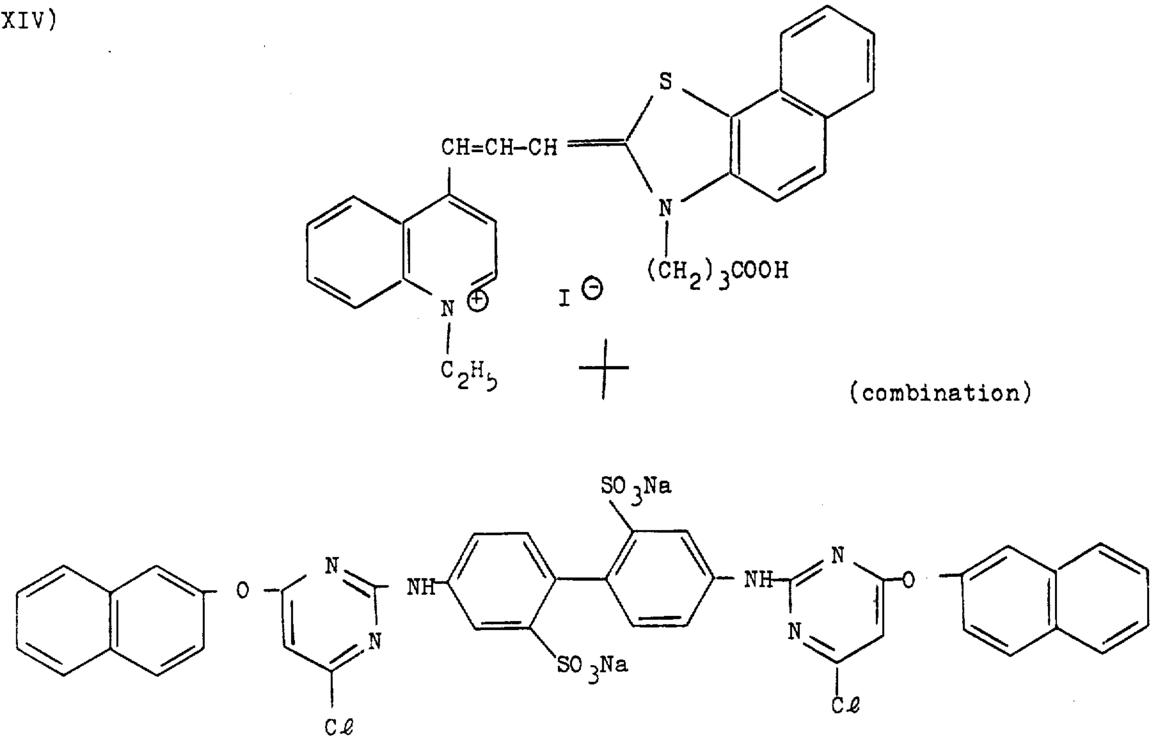

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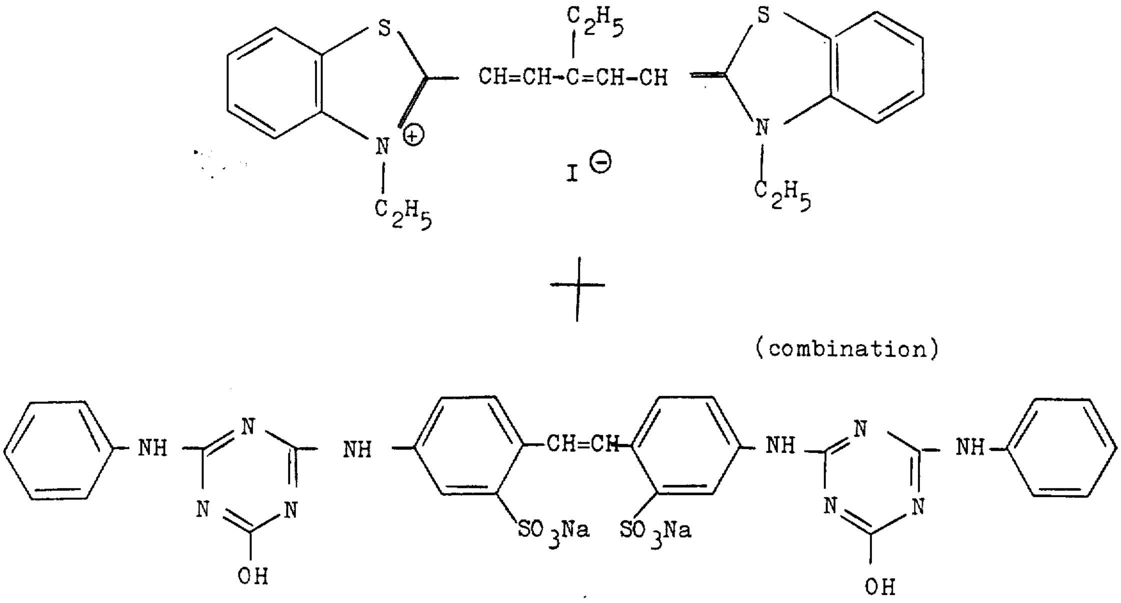

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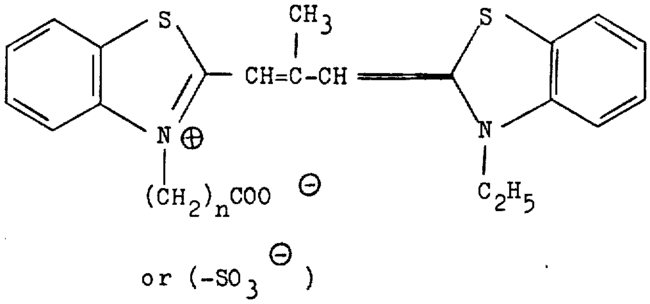

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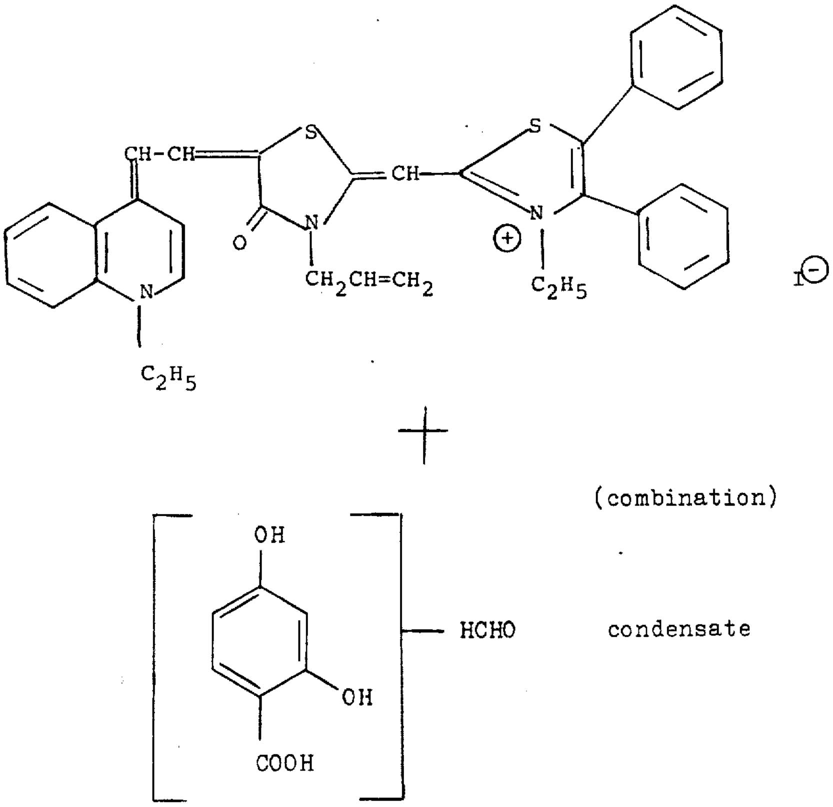

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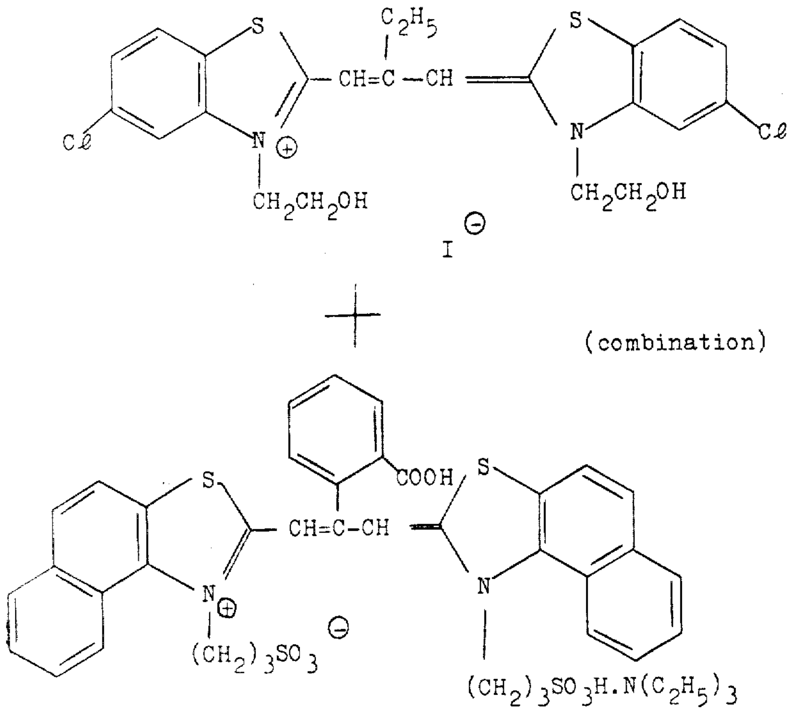


In addition, the photographic emulsion can contain an antifogging agent or a stabilizing agent which is known in the art. Examples of suitable stabilizing agents or antifogging agents are heterocyclic compounds such as 4-hydroxy-6-methyl-1,3,3a, 7-tetrazaindene, 3-methylbenzothiazole and 1-phenyl-5-mercaptotetrazole, mercury-containing compounds, mercapto compounds and metal salts as disclosed in CEK Mees *The Theory of The Photographic Process* Third Ed. (1966), U.S. Pat. Nos. 1,758,576; 2,110,178; 2,131,038; 2,173,628; 2,697,040; 2,304,962; 2,324,123; 2,394,198; 2,444,605~8; 2,566,245; 2,694,716; 2,697,099; 2,708,162; 2,728,633~5, 2,476,536; 2,824,001; 2,843,491; 2,886,437; 3,052,544; 3,137,577; 3,220,839; 3,226,231; 3,236,652; 3,251,691; 3,252,799; 3,287,135; 3,326,681; 3,420,668 and 3,622,339; British Pat. Nos. 893,428; 403,789; 1,736,609 and 1,200,188.

Furthermore, the photographic emulsion and/or the auxiliary layer used in the present invention can contain a hardener, such as an aldehyde, a formaldehyde precursor containing methylol group or alkylaminomethyl group, a 1,4-dioxane, an aziridine, an isoxazole, a carbodiimide, an active halogen containing compound or, an active vinyl compound; a gelatin plasticizer such as an aliphatic alcohol or a glycol; various surface active agents as a coating aid or as an antistatic agent as well known in the art; a ultraviolet absorbant; a fluorescent brightening agent; and antihalation dyes or filter dyes.

The present invention will now be illustrated in greater detail by reference to the following examples of both the process for preparing the gelatin derivative used in the present invention and examples of the present invention. Unless otherwise indicated in the examples given hereinafter, all parts, percents, ratios and the like, are by weight.

PRODUCTION EXAMPLE 1

Phenyl Isocyanate-Processed Gelatin (abbreviated as Gd-1):

118 Grams of lime-processed gelatin prepared from cow bone was dissolved in 650 ml of distilled water at 50°C and the resulting solution was cooled to 40°C. A solution prepared by dissolving 6 g of phenyl isocyanate in 20 ml of acetone was added thereto over a 20 minute period while adding thereto a 10% sodium hydroxide aqueous solution under sufficient stirring in order to mainain the pH of the solution at 9.5. After the addition of the isocyanate solution, stirring was continued for an additional 20 minutes while maintaining the temperature and the pH of the solution at the same levels. Thereafter, the pH of the solution was adjusted to 7 using dilute sulfuric acid (5 wt%) followed by lyophilization. Thus, 120 g of the gelatin derivative (Gd-1) as a solid was obtained.

PRODUCTION EXAMPLE 2

1-Phenylcarbamoylaziridine-Processed Gelatin (abbreviated as Gd-2):

700 Grams of the same gelatin as used in Production Example 1 was swollen in 7 liters of distilled water followed by heating to 45°C to dissolve. After adjusting the pH of the gelatin aqueous solution to 9.1 using a 6N sodium hydroxide aqueous solution, a solution prepared by dissolving 94.5 g of 1-phenylcarbamoylaziridine in 150 ml of dioxane was added thereto over 15 minutes. Then, while maintaining the solution temperature at 45°C, the above-described mixed solution was vigorously stirred for 1.5 hours. The pH values decreased to 8.0. After adjusting the pH of the reaction mixture to 6.5 using 6N sulfuric acid, lyophilization was effected to obtain 695 g of the gelatin derivative (Gd-2).

PRODUCTION EXAMPLE 3

Benzenesulfonyl Chloride-processed Gelatin (abbreviated as Gd-3):

360 Grams of lime-processed inert gelatin prepared from ossein was dispersed in 3.6 liters of distilled water to swell. Then, after dissolving it by heating to 40°C, the pH of the solution was adjusted to 9.5 using a 6N sodium hydroxide aqueous solution. To this solution was added 24.6 g of benzenesulfonyl chloride over a 10

minute period under stirring. Stirring was continued for an additional hour, during which the temperature of the reaction mixture was maintained at 45°C and the pH was maintained at 9.5 using a 6N sodium hydroxide aqueous solution. Then, after adjusting the pH of the reaction mixture to 6.5 using 6N sulfuric acid, the mixture was cool-set, cut into pieces and washed for 24 hours with cold water. After redissolving the pieces, the solution was subjected to lyophilization. Thus, 3.8 g of the gelatin derivative (Gd-3) was obtained.

PRODUCTION EXAMPLE 4

4-Methylbenzenesulfonyl Chloride-Processed Gelatin (Gd-4):

500 Grams of the same gelatin as used in Production Example 3 was dissolved in 4 liters of distilled water at 40°–50°C, and the pH of the solution was adjusted to 9 ± 0.1 using a 5 wt.% sodium hydroxide aqueous solution. A solution prepared by dissolving 25.5 g of 4-methylbenzenesulfonyl chloride in 100 ml of dioxane was added to the above-described gelatin aqueous solution over a 20 minute period under stirring while maintaining the temperature and the pH at the same levels. After the completion of the addition, the reaction mixture was stirred for 20 minutes at the same pH and the same temperature. Then, the solution was desalted by passing it through a mixed bed of a commercially available cation exchange resin (IR-120 produced by Organo Co. Ltd.) and a commercially available anion exchange resin (IR-45 produced by Organo Co. Ltd.). The pH of the solution, after desalting was adjusted to 6–7 using a dilute caustic aqueous solution. Upon condensing the solution and drying in warm air, 420 g of the gelatin derivative (Gd-4) was obtained.

PRODUCTION EXAMPLE 5

4-Methylbenzenesulfonyl Chloride-Processed Gelatin (Gd-5):

The same procedures as described in Production Example 4 were conducted except for changing the amount of 4-methylbenzenesulfonyl chloride from 25.5 g to 34 g and changing the desalting method (the same noodle washing as described in Production Example 3 being conducted instead of ion exchange resin-processing of Production Example 4). Thus, 425 g of the gelatin derivative (Gd-5) was obtained.

PRODUCTION EXAMPLE 6

3-Phenyloxy-1,2-epoxypropane-Processed Gelatin (Gd-6):

50 Grams of the same gelatin as used in Production Example 4 was dispersed in 500 g of water and dissolved at 55°C. To this solution was added a 10% sodium hydroxide aqueous solution to adjust the pH to 9. Then, 25 g of an acetone solution containing 10.8 g of 3-phenyloxy-1,2-epoxypropane was added thereto over a 1 hour period, during which a 10% sodium hydroxide aqueous solution was added incrementally thereto so as to maintain the pH at 9. After the addition of the epoxide, stirring was continued for an additional 2 hours at 55°C. After adjusting the pH of the reaction mixture to 7 by adding a 5% sulfuric acid aqueous solution, the reaction mixture was gradually poured into 2 liters of acetone under stirring. The precipitate formed was collected by filtration and air-dried. Thus, 45 g of the gelatin derivative (Gd-6) was obtained.

PRODUCTION EXAMPLE 7

Phthalic Anhydride-Processed Gelatin (Gd-7):

100 Grams of the same gelatin as used in Production Example 4 was dispersed in 1 liter of distilled water and dissolved at 40°C. To this solution was added a 10% sodium hydroxide aqueous solution under stirring to adjust the pH to 10. 7 Grams of phthalic anhydride, dissolved in 50 g of acetone, was added to the above-described gelatin aqueous solution over about a 15 minute period, during which the temperature and the pH of the reaction mixture were maintained at 40°C and 10, respectively. After the completion of the addition, the reaction mixture was stirred for an additional 10 minutes. Then, after adjusting the pH of the solution to 7 with dilute (5 wt.%) sulfuric acid, the reaction mixture was cool-set to gel. After cutting, it was washed and dried. Thus, 82 g of the gelatin derivative (Gd-7) was obtained.

EXAMPLES 1 – 10

The materials used in the following Examples 1 to 10 are given in Tables 1 to 7.

Table 1

Color Former	Name*
No. 1	2'-Chloro-5'-[2-(2,4-di-5-pentylphenoxy)butylamido]-4-methoxybenzoylacetanilide
No. 2	2'-Chloro-5'-[2-(2,4-di-5-pentylphenoxy)butylamido]-α-(5,5-dimethyl-3-hydantoinyl)-2-(4-methoxybenzoyl)acetanilide
No. 3	1-(2,4,6-Trichlorophenyl)-3- 3-[(2,4-di-t-pentylphenoxy)acetamido]benzamido -4-(4-methoxyphenyl)azo-2-pyrazol-5-one
No. 4	1-(2,4,6-Trichlorophenyl)-3- 3-[(2,4-di-t-pentylphenoxy)acetamido]benzamido-2-pyrazol-5-one
No. 5	1-(2,6-Dichloro-4-methoxyphenyl)-3- 3-[2-(2,4-di-t-pentylphenoxy)butylamido]benzamido -2-pyrazol-5-one
No. 6	1-Hydroxy-4-chloro-N-dodecyl-2-naphthamide
No. 7	2,4-Dichloro-3-methyl-6-[2-(2,4-di-t-pentylphenoxy)butylamido]phenol
No. 8	1-Hydroxy-4-(2-acetylphenyl)azol-N-[4-(2,4-di-t-pentylphenoxy)butyl]2-naphthamide
No. 9	1-Hydroxy-N-dodecyl-2-naphthamide

*According to "Waei Yuki-kagaku Meimeiho(Zen) (Japanese-English Organic Chemical Nomenclature (complete): by Hirayama and Hirayama (1972)) (hereinafter the same).

Table 2

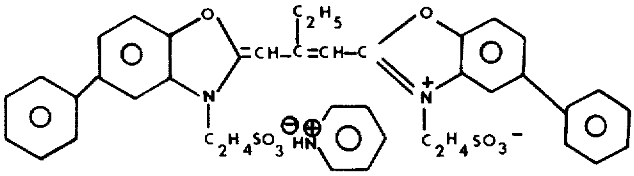
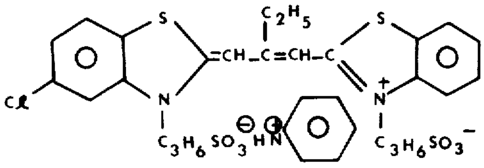
Spectral Sensitizing Agent	Structural Formula
No. 1	
No. 2	

Table 3

Stabilizing Agent	Name*
No. 1	4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene
No. 2	N-Methylbenzothiazolium Iodide
No. 3	1-Phenyl-5-mercaptotetrazole

Table 4

Hardener	Name*
No. 1	Mucochloric Acid
No. 2	3-Chloro-2-phenoxymalealdehydic Acid
No. 3	2,4-Dichloro-6-hydroxyl-1,3,5-triazine Sodium Salt
No. 4	1,3,5-Triacryloylhexahydro-1,3,5-triazine
No. 5	2,3-Dihydroxy-5-methyl-1,4-dioxane
No. 6	Formaldehyde

Table 5

Matting Agent	Name
No. 1	Strontium Barrium Sulfate Grains
No. 2	Silver Halide Grains
No. 3	Silicon Dioxide Grains
No. 4	Polymethyl Methacrylate Grains

Table 6

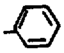
Coating Aid	Name* or Structural Formula
No. 1	Sodium p-Dodecylbenzenesulfonate
No. 2	2-Sulfonato.succinic Acid bis(2-Ethylhexyl)-ester Sodium Salt
No. 3	Dimethyltetradecylammonioacetate (internal salt)
No. 4	Dimethyldodecylammonioacetate (internal salt)
No. 5	C_9H_{19}  $-O-(CH_2CH_2O)_n-(CH_2)_m-SO_3Na$ n = 0 – 15 m = 3 or 4

Table 7

Anti-Friction Agent	Name
No. 1	Liquid Paraffin
No. 2	Cetyl Palmitate
No. 3	Silicone Oil

The kinds and the structures of the emulsion layers used in the examples and additives incorporated in each layer are as follows.

Light-Sensitive Material No. 1 (color negative film) comprising:

Base: triacetyl cellulose (hereinafter abbreviated as TAC);

Subbing Layer: containing gelatin, salicylic acid, acetone, methanol, methylene chloride and water;

Antihalation Layer (hereinafter abbreviated as AH layer): containing black colloidal silver, gelatin, water and Hardener No. 2;

Red-Sensitive Layer (hereinafter abbreviated as RL): a gelatino-silver bromoiodide emulsion (containing 7 mol% of silver iodide) containing Color Former No. 8, Color Former 9, Sensitizing Dye No. 2, Stabilizing Agent No. 1, Hardener No. 2 and Coating Aid No. 1;

Gelatin Intermediate Layer: containing Coating Aid No. 1 and Coating Aid No. 5, Hardener No. 2 and lime-processed gelatin;

Green-Sensitive Layer (hereinafter abbreviated as GL): a gelatino-silver bromoiodide emulsion layer (containing 7 mol% of silver iodide) containing Color Former No. 3 and Color Former No. 4, Sensitizing Dye No. 1, Stabilizing Agent No. 1, Hardener No. 2 and Coating Aid No. 1;

Yellow Filter Layer (hereinafter abbreviated as YF layer): containing coating Aid No. 1, Hardener No. 2, colloidal silver and lime-processed gelatin; and

Blue-Sensitive Layer (hereinafter abbreviated as BL): a gelatino-silver bromoiodide emulsion layer (containing 7 mol% of silver iodide) containing Color Former No. 2, Stabilizing Agent No. 1, and Hardener No. 2.

Light-sensitive Material No. 2 (coupler-in-emulsion color reversal film) comprising:

Base: TAC:

Subbing Layer: containing gelatin, salicyclic acid, acetone, methanol, methlene chloride and water;

AH Layer: containing black colloidal silver, gelatin, water and Hardener No. 2;

RL: a gelatino-silver bromoiodide emulsion layer (containing 0.5 mol% of silver iodide) containing

Color Former No. 9, Spectral Sensitizing Agent No. 2, Stabilizing Agent No. 1, Hardener No. 3 and Coating Aid No. 1;

Gelatin Intermediate Layer: containing Hardener No. 3 and Coating Aid No. 1;

GL: a gelatino-silver bromoiodide emulsion layer (containing 0.8 mol% of silver iodide) containing Color Former No. 4, Spectral Sensitizing Agent No. 1, Stabilizing Agent No. 1, Hardener No. 3, and Coating Aid No. 1;

YF Layer: containing Hardener No. 3, Coating Aid No. 1 and colloidal silver; and

BL: a gelatino-silver bromoiodide emulsion layer (containing 1 mol% of silver iodide) containing Color Former No. 1, Stabilizer No. 1, Hardener No. 3, and Coating Aid No. 1.

Light-Sensitive Material No. 3 (color positive film) comprising:

Base: TAC:

Subbing Layer: containing gelatin, salicylic acid, acetone, methanol, methylene chloride and water;

BL: a gelatino-silver bromoiodide emulsion layer (containing 1.2 mol% of silver iodide) containing Color Former No. 1, Stabilizer No. 1 and Stabilizer No. 2, Hardener No. 3, Coating Aid No. 1 and Coating Aid No. 5;

Gelatin Intermediate Layer: containing Hardener No. 3, Coating Aid No. 1 and Coating Aid No. 5;

RL: a gelatino-silver chlorobromide emulsion layer (containing 45 mol% of silver bromide) containing Color Former No. 6, Spectral Sensitizing Agent No. 2, Stabilizer No. 1, Stabilizer No. 2, Hardener No. 3, Coating Aid No. 1 and Coating Aid No. 5;

Gelatin Intermediate Layer: containing Hardener No. 3, Coating Aid No. 1 and Coating Aid No. 5; and

GL: a gelatino-silver chlorobromide emulsion layer (containing 45 mol% of silver bromide) containing Color Former No. 4, Spectral Sensitizing Agent No. 1, Stabilizing Agent No. 1, Stabilizing Agent No. 2, Hardener No. 3, Coating Aid No. 1 and Coating Aid No. 5.

Light-Sensitive Material No. 4 (color paper) comprising:

Base: polyethylene-coated paper;

Subbing Layer: containing gelatin, ethanol and water;

BL: a gelatino-silver chlorobromoiodide emulsion layer (containing 1 mol% of silver iodide) containing Color Former No. 1, Stabilizer No. 1, Hardener No. 3, Hardener No. 4 and Coating Aid No. 1;

Gelatin Intermediate Layer: containing Hardener No. 3, Hardener No. 4, and Coating Aid No. 1;

GL: a gelatino-silver chlorobromide emulsion layer (containing 40 mol% of silver bromide) containing Color Former No. 5, Spectral sensitizing Agent No. 1, Stabilizing Agent No. 1, Hardener No. 3, Hardener No. 4 and Coating Aid No. 1;

Ultraviolet Ray-Absorbing Layer: containing an ultraviolet ray-absorbing agent of tinuvin series (compound described in U.S. Pat. No. 3,533,794 was used in the manner described therein), Hardener No. 3, Hardener No. 4 and Coating Aid No. 1; and

RL: a gelatino-silver chlorobromide emulsion layer (containing 50 mol% of silver bromide) containing Color Former No. 7, Spectral sensitizing Agent No. 2, Stabilizing Agent No. 1, Hardener No. 3, Hardener No. 4 and Coating Aid No. 1.

Light-Sensitive Material No.5(coupler-free reversal color film) comprising:

Base: polyethylene terephthalate;

Subbing Layer: containing gelatin, salicyclic acid, nitrocellulose, methylene chloride, acetone, phenol and water;

RL: a gelatino-silver bromoiodide emulsion layer (containing 1 mol% of silver iodide) containing Spectral Sensitizing Agent No. 2, Stabilizing Agent No. 1, Stabilizing Agent No. 3, Hardener No. 6 and Coating Aid No. 1;

GL: a gelatino-silver bromoiodide emulsion layer (containing 4 mol% of silver iodide) containing Spectral Sensitizing Agent No. 1, Stabilizing Agent No. 1, Stabilizing Agent No. 3, Hardener No. 6 and Coating Aid No. 1;

YF Layer: containing Hardener No. 6, Coating Aid No. 1 and colloidal silver; and

BL: a gelatino-silver bromoiodide emulsion layer (containing 4 mol% of silver iodide) containing Stabilizing Agent No. 1, Stabilizing Agent No. 3, Hardener No. 6 and Coating Aid No. 1.

The processing temperatures, processing periods of time and compositions of the processing solutions used in the samples are given below.

Processing No. 1:		
Color Development	1'30"	52°C
Rinsing	15"	
Bleach-Fixation	1'30"	
Washing with Water	1'30"	
Stabilizing	10"	
Rinsing	5"	

As the compositions of the processing solutions, those for color positive materials of those described in *Journal of the Society of Motion Picture and Television Engineers*, 61, pp.667–701 (1953) were employed per se, as follows:

Color Print Developer (Kodak SD-31)	
Water (about 21–24°C)	800 ml
Sodium Metaphosphate, Sodium Hexametaphosphate or Calgon(Calgon, Inc.)	2.0 g
Sodium Sulfite (desicated)	4.0 g
2-Amino-5-diethylaminotoluene Monohydro-chloride	3.0 g
Sodium Carbonate (monohydrated)	2.0 g
Water to make	1.0 liter
pH(70F), 10.65±0.05	
Specific gravity (70F), 1.023±0.003	

Processing No. 2:		
Color Development (containing p-phenylenediamine color developing agent and bromide)	3'3"	31°C
Bleach-Fixing (containing EDTA-iron salt and thiosulfate)	3'	
Washing with Water	3'	
Stabilizing Bath (containing a buffer agent)	3'	
Processing No. 3:		
Color Development	6'	30°C
Stop-Fixing	2'	"
Washing with Water	2'	27°C
Bleaching	2'	30°C
Washing with Water	2'	27°C
Hardening and Fixing	4'	30°C
Washing with Water	4'	27°C
Stabilizing	2'	30°C
Rinsing	1'	27°C

The compositions of the processing solutions were the same as described in *The British Journal of Photography*, 1968, Oct. 27th number, pp.838–840 as follows: The compounds were dissolved in the order indicated, at a maximum temperature of 35°C.

Color Developer	
Sodium Metaborate	25.0 g
Sodium Sulphite (anhydrous)	2.0 g
Hydroxylamine (sulfate or hydrochloride)	2.0 g
Potassium Bromide	0.5 g
6-Nitrobenzimidazole Nitrate	0.02 g
Caustic soda, pellets	4.0 g
Benzyl Alcohol Solution*	45.0 cc
	(pH - 10.6)
Added before use:	
KODAK CD-3	8.0 g (or 40 cc 20% solution)**
Water to	1000 cc
* Composition as follows:	
Benzyl Alcohol	35.0 cc
Diethylene Glycol	45.0 cc
Water to	100.0 cc
** Composition as follows:	
CD-3	20.0 g
Potassium Metabisulphite	2.0 g
Water to	100.0 cc
Stop-Fix	
Ammonium Thiosulphate	120.0 g
Potassium Metabisulphite, (cryst.)	20.0 g
Acetic Acid (glacial)	10.0 cc
Water to	1000 cc
	(pH: 4.5)
Bleach	
Sodium or Potassium Nitrate, (cryst.)	25.0 g
Potassium Ferricyanide	20.0 g
Potassium Bromide	8.0 g
Boric Acid (cryst.)	5.0 g
Borax	2.5 g
or Sodium Metaborate	1.5 g
Water to	1000 cc
	(pH: 7.2)
Hardener-Fixer	
Ammonium Thiosulphate (cryst.)	120.0 g
Sodium Sulphite (anhydrous)	5.0 g
Boric Acid (cryst.)	2.5 g
Formaldehyde (35–40%)	40.0 cc
Water to	1000 cc
	(pH: 9.5)
Stabilizer	
Zinc Sulphate (cryst.)	10.0 g
Tartaric Acid	10.0 g
Sodium Metaborate	20.0 g
Water to	1000 cc
	(pH: 9.5)

Processing No. 4:		
Color Development	1'10"	65°C
Rinsing	10"	
Bleach-Fixing	1'10"	
Washing with Water	1'10"	
Stabilizing	10"	
Rinsing	2"	

The compositions of the processing solutions were the same as used in Processing No. 1.

Processing No. 5:		
Color Development	2'	38°C
Rinsing	15"	
Bleach-Fixing	2'	
Washing with Water	2'	
Stabilizing	15"	
Rinsing	5"	
Processing No. 6:		
Pre-hardening	1'	37°C
Neutralizing	30"	
Black-and-white Development	3'20"	
First Stopping	30"	
Washing	1'	
Color Development	5'30"	
Second Stopping	1'	
Washing	2'	
Bleaching	1'30"	
Fixing	1'30"	
Washing with Water	1'30"	

The compositions of the processing solutions were the same as those for the coupler-in-emulsion reversal films described in U.S. Patent 3,723,125, except that the compositions of the first and the second stopping baths were as follows.

Glacial Acetic Acid	30 ml
Sodium Hydroxide	3.2 g
Water	Up to 1 liter

Processing No. 7:

The steps were exactly the same as used in Processing No. 6, except that the processing temperature was 50°C throughout the steps. The compositions of the processing solutions were also the same as used in Processing No. 6.

Processing No. 8:

The steps were the same as used in Processing No. 6, except that the pre-hardening and the neutralizing steps were omitted (the processing temperature of 37°C was the same as in Processing No. 6). The compositions of the processing solutions were also the same as used in Processing No. 6.

Processing No. 9:

The steps were the same as used in Processing No. 8, except that the processing temperature was 50°C throughout the steps. The compositions of the processing solutions were also the same as used in Processing No. 8, therefore, Processing No. 6.

Processing No. 10:		
Color Development	2'30"	38°C
Bleaching	6'	
Washing with Water	3'	
Fixing	6'	
Washing with Water	3'	
Stabilizing	3'	

The compositions of the processing solutions are described after Processing No. 11.

Processing No. 11:

The steps were the same as used in Processing No. 10, except that the processing temperature was 46°C throughout all of the steps. The compositions of the processing solutions were also the same as used in Processing No. 10. Compositions of the processing solutions in Processing Nos. 10 and 11:

Color Developer	
Sodium Sulfate	2.0 g
Sodium Carbonate (monohydrate)	30.0 g
Potassium Bromide	2.0 g
Benzyl Alcohol	5.0 ml
Hydroxylamine Sulfate	1.6 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline Sulfate	4.0 g
Water to make the total	1 liter
Bleaching Solution	
Iron-ethylenediaminetetraacetic Acid Sodium Salt	100.0 g
Potassium Bromide	60.0 g
Ammonium Hydroxide (28%)	50.0 ml
Glacial Acetic Acid	25.0 ml
Water to make the total	1 liter
Fixing Solution	
Sodium Sulfate	10.0 g
Sodium Thiosulfate	200.0 g
Water to make the total	1 liter
Stabilizing Solution	
Formalin (40%)	10.0 ml
Water to make the total	1 liter

Processing No. 12:		
Pre-hardening	1'	
Washing with Water	1'	
Negative Development	4'	
Washing with Water	3'	
Reversal-Red Flash Exposure-Cyan Color Development	5'	
Washing with Water	5'	27°C throughout all of the steps except
Reversal Blue Flash Exposure		
Yellow Color Development	5'	for the exposure
Washing with Water	2'	steps
Reversal White Light Exposure Magenta Color Development	5'	
Washing with Water	2'	
Bleaching	5'	
Fixing	3'	

The compositions of the processing solutions were the same as those for the coupler-free reversal color film described in U.S. Pat. No. 3,723,125.

Processing No. 13:

The steps were the same as used in Processing No. 12, except that the processing temperature was 30°C throughout all steps. The compositions of the processing solutions were also the same as used in Processing No. 12.

Processing No. 14 (for comparison):		
Color Development	12′	24°C
Bleaching	10′	
Washing	4′	
Fixing	10′	
Washing with Water	8′	
Stabilizing	4′	

The compositions of the processing solutions were the same as used in Processing Nos. 10 and 11.

EXAMPLE 1

The Light-Sensitive Material No. 3 was used, on which each protective layer having the composition given in Table 8 (further containing 100 g of COating Aid No. 1 (1%) and Anti-Friction Agent No. 1) was coated as the uppermost layer and dried. (The thickness of the protective layer was 1–2μ after drying.) The thus obtained Samples 1a–1f were processed according to Processing No. 1. The degrees of reticulation obtained are given in Table 9, and the photographic properties (relative sensitivity and fog) are shown in Table 10.

Table 8

Sample	Gelatin Used in Protective Layer	Hardener
1a	7% Aqueous Solution of Lime-Processed Gelatin: 1000 g	None
1b	″	No. 3(2%): 20 g
1c	7% Aqueous Solution of Gd-3. 1000 g	″
1d	″	No. 3(2%): 12 g
1e	″	No. 3(2%): 4 g
1f	″	None

Table 9

Sample	Reticulation
1a	E
1b	D
1c	A
1d	A
1e	B
1f	D

The degrees of reticulation were rated according to the following criteria.

A: No reticulation was observed.

B: Reticulation was slightly observed using an optical microscope of 200 magnification, though not observed using the naked eye.

C: Reticulation was slightly observed using the naked eye.

D: Reticulation was considerably observed using the naked eye.

E: Reticulation occurred all over and delamination was about to take place.

In the following examples, grades A to E are as set forth above.

Table 10

Sample	Relative Sensitivity Taking 1b as 100			Fog		
	RL	GL	BL	RL	GL	BL
1a	110	112	104	0.10	0.13	0.10
1b	100	100	100	0.10	0.12	0.10
1c	96	121	94	0.10	0.12	0.10
1d	100	123	98	0.10	0.12	0.10
1e	104	122	102	0.10	0.12	0.10
1f	106	125	107	0.10	0.12	0.10

From a comparison of the results given in Table 9, it can be seen that reticulation clearly occurs with difficulty when the gelatin derivative is used for the uppermost layer in place of ordinary lime-processed gelatin. From Table 10, no tendency for fog to increase by using the gelatin derivative for the uppermost layer was observed and, as to sensitivity, the sensitivity of the green-sensitive layer lying immediately under the protective layer is seomwhat high, which is quite preferable. This may be attributed to the fact that the swelling degree of the uppermost layer in the vertical direction is increased. (The results should be comparatively examined from the stand point of not only the reticulation-preventing effects but also from the standpoint of the improvement in photographic properties (e.g., sensitivity, fog, etc.)).

EXAMPLE 2

Light-Sensitive Material No. 4 was used, on which each protective layer having the composition given in Table 11 (further containing 60 g of Coating Aid No. 1 (1%), 20 g of Coating Aid No. 2 (2%), and Anti-Friction Agent No. 1) was coated and dried (the thickness of the protective layer after drying being 1–2μ). The thus obtained Samples 2a–2i were processed according to Processings No. 2 and No. 3. The degrees of reticulation in this occasion are given in Table 12.

Table 11

Sample	Gelatin Used in Protective Layer	Hardener
2a	7% Aqueous Solution of Lime-Processed Gelatin: 1000 g	No. 3 (2%): 12 g
2b	″	No. 3(2%): 8 g. No. 4(1%): 16 g
2c	″	No. 4 (1%): 32 g
2d	7% Aqueous Solution of Gd-4: 1000 g	No. 3 (2%): 12 g
2e	″	No. 3 (2%): 8 g No. 4 (1%): 16 g
2f	″	No. 4 (1%): 32 g
2g	7% Aqueous Solution of Gd-5: 1000 g	No. 3 (2%): 12 g
2h	″	No. 3 (2%): 8 g No. 4 (1%): 16 g
2i	″	No. 4 (1%): 32 g

Table 12

Sample	Reticulation	
	Processing No. 2	Processing No. 3
2a	D	C
2b	D	C
2c	E	D
2d	A	A
2e	A	A
2f	C	B
2g	A	A
2h	A	A
2i	C	B

From a comparison of the results given in Table 12, it can be seen that reticulation occurs with difficulty by using the gelatin derivative for the uppermost layer as compared with the case of using ordinary lime-processed gelatin. It can also be seen that this effect does not depend upon the kind of hardener used.

EXAMPLE 3

Light-Sensitive Material No. 3 was used, on which one of 3a–3c was coated.

3a: An aqueous solution containing 20 g of Hardener No. 3 (2%) and 1000 g of Coating Aid No. 1 (1%) per 100 g of a 7% aqueous solution of lime-processed gelatin was applied in a dry thickness of 2 microns as a protective layer.

3b: An aqueous solution containing 8 g of Hardener No. 3 (2%) and 100 g of Coating Aid No. 1 (1%) per 1000 g of a 7% aqueous solution of Gd-2was coated on the protective layer 3a in a dry thickness of 1 micron.

3c: Protective layer 3a was provided in a thickness of 1 μ, and an aqueous solution containing 8 g of Hardener 3 (2%) and 100 g of Coating Aid No. 1 (1%) per 1000 g of a 7% aqueous solution of Gd-2 was coated thereon in a dry thickness of 1 μ.

After coating and drying, the resulting samples were stored at 25°C and 60% RH for 7 days, and then processed according to Processing No. 5. The degrees of reticulation at this time are given in Table 13.

Table 13

Sample	Reticulation
3a	D
3b	B
3c	B

From the results in Table 13, it can be seen that reticulation can be significantly reduced by coating the gelatin derivative on an ordinary protective layer.

EXAMPLE 4

Light-Sensitive Material No. 2 was used, on which a coating layer having the composition shown in Table 14 (further containing 10 g of Matting Agent No. 2 and 4 g of Matting Agent No. 4, and Anti-Friction Agent No. 1) was coated as the uppermost layer and dried (the thickness of the protective layer after drying being 0.5–1 μ). The thus obtained Samples 4a–4h were processed according to Processings No. 6 and No. 7. The degrees of reticulation upon processing are shown in Table 15.

Table 14

Sample	Gelatin Used in Protective Layer	Hardener	Coating Aid
4a	5% Aqueous Solution of Lime-Processed Gelatin: 1500 g	None	No. 1 (1%): 100 g No. 3 (2%): 20 g
4b	''	No. 2 (2%): 80g	''
4c	5% Aqueous Solution of Gd-6: 1500 g	None	''
4d	''	No. 2 (2%): 80g	No. 1 (1%): 100 g No. 3 (2%): 20 g
4e	5% Aqueous Solution of Gd-1: 1500 g	None	''
4f	''	No. 2 (2%): 80 g	''
4g	5% Aqueous Solution of Gd-7: 1500 g	None	No. 1 (1%): 100 g No. 3 (2%): 20 g No. 4 (2%): 5 g
4h	''	No. 2 (2%): 80g	''

Table 15

Sample	Reticulation	
	Processing No. 6	Processing No. 7
4a	E	Delaminated
4b	D	E
4c	D	E
4d	C	C
4e	C	D
4f	A	B
4g	D	E
4h	B	C

From a comparison of the results given in Table 15, it can be seen that, even in the processing involving a hardening step (i.e., pre-hardening processing), reticulation is made difficult to occur by using the gelatin derivative instead of ordinary gelatin.

EXAMPLE 5

Light-Sensitive Material No. 2 was used, on which each protective layer having the composition given in Table 16 (further containing 100 g of Coating Aid No. 1 (1%), 10 g of Matting Agent No. 3, and Anti-Friction Agent No. 2) was coated as the uppermost layer and dried. The thus obtained samples 5a–5h were processed according to Processings No. 8 and No. 9. The degrees of the reticulation upon processing are shown in Table 17.

Table 16

Sample	Gelatin Used in Protective Layer	Hardener
5a	5% Aqueous Solution of Lime-Processed Gelatin: 1500 g	No. 1 (2%): 80 g
5b	''	No. 5 (2%): 40 g
5c	5% Aqueous Solution of Gd-2: 1500 g	No. 1 (2%): 80 g
5d	''	No. 5 (2%): 40 g
5e	5% Aqueous Solution of Gd-3: 1500 g	No. 1 (2%): 80 g
5f	''	No. 5 (2%): 40 g
5g	5% Aqueous Solution of Gd-5: 1500 g	No: 1 (2%): 80 g
5h	''	No. 5 (2%): 40 g

Table 17

Sample	Reticulation	
	Processing No. 8	Processing No. 9
5a	D	E
5b	D	E
5c	B	B
5d	A	A
5e	A	B
5f	A	A
5g	B	B
5h	A	B

From the results given in Table 17, it can be seen that, even when the hardeners are different, reticulation is clearly made difficult to occur by using the gelatin derivative. In addition, the sensitivity of these samples was determined taking Sample 5a as a control for Samples 5c, 5e and 5g and taking Sample 5b as a control for Samples 5d, 5f and 5h. With Samples 5c–5h, RL and GL had the same sensitivity and BL had a somewhat, high sensitivity, which was very preferable. (Too high a sensitivity is not preferable.) With fog, substantially the same results were obtained with these samples.

EXAMPLE 6

Light-Sensitive Material No. 1 was used, on which each protective layer having the composition given in Table 18 (further containing 60 g of Coating Aid No. 1 (1%), 60 g of Coating Aid No. 2 (1%), 60 g of Matting

Agent No. 1, 4 g of Matting Agent No. 4, and Anti-Friction Agent No. 1) was coated as the uppermost layer and dried (the thickness of the resulting protective layer after drying being 1–2μ). The thus obtained Samples 6a–6i were processed according to Processings No. 10, No. 11 and No. 14. The degrees of reticulation are shown in Table 19.

Table 18

Sample	Gelatin Used in Protective Layer	Hardener
6a	5% Aqueous Solution of Lime-Processed Gelatin: 1500 g	No. 3 (2%): 20 g
6b	5% Aqueous Solution of Lime-Processed Gelatin: 1200 g; 5% Aqueous Solution of Gd-2: 300 g	No. 3 (2%): 20 g
6c	5- Aqueous Solution of Lime-Processed Gelatin: 900 g; 5% Aqueous Solution of Gd-2: 600 g	No. 3 (2%): 20 g
6d	5% Aqueous Solution of Lime-Processed Gelatin: 600 g; 5% Aqueous Solution of Gd-2: 900 g	"
6e	5% Aqueous Solution of Gd-2: 1500 g	"
6f	5% Aqueous Solution of Lime-Processed Gelatin: 1200 g; 5% Aqueous Solution of Gd-3: 300 g	"
6g	5% Aqueous Solution of Lime-Processed Gelatin: 900 g; 5% Aqueous Solution of Gd-3: 600 g	No. 3 (2%): 20 g
6h	5% Aqueous Solution of Lime-Processed gelatin: 600 g; 5% Aqueous Solution of Gd-3: 900 g	"
6i	5% Aqueous solution of Gd-3: 1500 g	"

Table 19

Sample	Reticulation		
	Processing No. 10	Processing No. 11	Processing No. 14 (for comparison)
6a	E	Delaminated	A
6b	C	D	A
6c	A – B	B	A
6d	A	A	A
6e	A	A	A
6f	C	D	A
6g	B	B	A
6h	A	A	A
6i	A	A	A

The following conclusions can be drawn from the above results:

1. Even with samples where a gelatin-gelatin derivative mixture (mixing ratio: 8:2) was used as the uppermost layer, reticulation was made difficult to occur as compared with the case of using ordinary gelatin alone (common to Processings No. 10 and No. 11).

2. The effects of using the gelatin derivative were clearly observed in processing at a high temperature of 38°C or 46°C, although not observed in the processing at 24°C (Processing No. 14).

3. With sample 6a wherein ordinary gelatin was used as the protective colloid, processing at a temperature as high as 38°C (Processing No. 10) was impossible due to serious reticulation. However, the gelatin derivative enables the conducting of the high temperature processing, which serves to greatly shorten the processing time. (With Processing No. 14, the processing time was 48', while with Processing No. 10, it was 23'30".)

EXAMPLE 7

On each of the following light-sensitive materials (A) to (D) was applied a protective layer having the composition given in Table 20 (further containing 60 g of Coating Aid No. 1 (1%), 60 g of Coating Aid No. 2 (1%), 10 g of Matting Agent No. 1 and 4 g of Matting Agent No. 4) and dried. The thus obtained samples 7a–7h were processed according to Processings No. 10 and No. 11. The degree of reticulation upon processing are shown in Table 21.

A: Light-Sensitive Material No. 1 was used per se.

(B): The light-sensitive material was prepared by replacing gelatin in the YF layer of Light-Sensitive Material No. 1 completely with Gd-2.

(C): The light-sennsitive material was prepared by replacing gelatin in the intermediate layer of Light-Sensitive Material No. 1 completely with Gd-2.

(D): The light-sensitive material was prepared by completely replacing gelatin in both the YF layer and the gelatin intermediate layer of Light-Sensitive Material No. 1 with Gd-2.

Table 20

Sample	Emulsion Used	Gelatin Used in Protective Layer	Hardener
7a	(A)	5% Aqueous Solution of Lime-Processed Gelatin: 1500 g	No. 2 (2%): 80 g
7b	(A)	5% Aqueous Solution of Gd-2: 1500 g	"
7c	(B)	5% Aqueous Solution of Lime-Processed Gelatin: 1500 g	"
7d	(B)	5% Aqueous Solution of Gd-2: 1500 g	"
7e	(C)	5% Aqueous Solution of Lime-Processed Gelatin: 1500 g	"
7f	(C)	5% Aqueous Solution of Gd-2: 1500 g	"
7g	(D)	5% Aqueous Solution of Lime-Processed Gelatin: 1500 g	"
7h	(D)	5% Aqueous Solution of Gd-2: 1500 g	"

Table 21

Sample	Reticulation	
	Processing No. 10	Processing No. 11
7a	D	E
7b	A	A
7c	C	D
7d	A	A
7e	D	E
7f	A	A
7g	C	D
7h	A	A

From the results given in Table 21, it can be seen that, with Samples 7c, 7e and 7g wherein the gelatin in the intermediate layer and/or the YF layer was replaced by the gelatin derivative but the gelatin in the uppermost layer was not replaced, the effect of making it difficult for reticulation to occur was not observed at all, or, if observed, it was extremely small. It can also be seen that the use of the gelatin derivative in the uppermost layer sufficiently provides the effect of preventing reticulation, even when the intermediate layer and/or the YF layer is of ordinary gelatin.

EXAMPLE 8

Light-Sensitive Material No. 5 was used, to which each protective layer having the composition given in Table 22 (further containing 10 g of Matting Agent No. 3, Anti-Friction Agent No. 3) was applied as the uppermost layer and dried (the thickness of the protective layer after drying being 0.5–1.5μ). The thus obtained Samples 8a–8h were processed according to Processings No. 12 and No. 13. The degrees of reticulation upon processing are shown in Table 23.

Table 22

Sample	Gelatin Used in Protective Layer	Hardener	Coating Aid
8a	5% Aqueous Solution of Lime-Processed Gelatin: 1500 g	No. 6 (2%): 15 g	No. 1 (1%): 100 g
8b	5% Aqueous Solution of Gd-1: 1500 g	"	No. 1 (1%):60 g; No. 3 (2%): 40 g
8c	5% Aqueous Solution of Gd-2: 1500 g	"	"
8d	5% Aqueous Solution: of Gd-3: 1500 g	"	"
8e	5% Aqueous Solution of Gd-4: 1500 g	"	"
8f	5% Aqueous Solution of Gd-5: 1500 g	"	"
8g	5% Aqueous Solution of Gd-6 1500 g	"	"
8h	5% Aqueous Solution of Gd-7: 1500 g	"	"

Table 23

Sample	Reticulation	
	Processing No. 12	Processing No. 13
8a	A – B	D
8b	A	A
8c	A	A
8d	A	A
8e	A	A
8f	A	A
8g	A	B
8h	A	B

From the results given in Table 23, it can be seen that, in Processing No. 12 (temperature: 27°C), almost no difference was observed in the degree of reticulation between Sample 8a wherein ordinary gelatin was used as the uppermost layer and Samples 8b–8h wherein the gelatin derivative was used, but, in Processing No. 13 (temperature: 30°C), a great difference resulted therebetween. In addition, as to the photographic properties, the fog was the same in all cases and the relative sensitivity of Samples 8b–8h based on that of Sample 8a was preferable because the BL showed a somewhat high sensitivity in every case.

EXAMPLE 9

Light-Sensitive Material No. 1 was used, on which each of the protective layers having the composition given in Table 24 (further containing 60 g of Coating Aid No. 1 (1%), 60 g of Coating Aid No. 2 (1%), 10 g of Matting Agent No. 1, 4 g of Matting Agent No. 4 and Anti-Friction Agent No. 1) was coated as the uppermost layer and dried. The thus obtained Samples 9a–9e were processed according to Processings No. 10 and No. 11.

The degrees of reticulation upon processing are shown in Table 25, and the relative sensitivity and fog of each sample in Table 26.

Table 24

Sample	Gelatin Used in Protective Layer	Hardener
9a	5% Aqueous Solution of Lime-Processed Gelation: 1500 g	No. 2 (10%): 96 g
9b	"	No. 2 (10%): 48 g
9c	"	No. 2 (2%): 80 g
9d	5% Aqueous Solution of Gd-2: 1500 g	"
9e	5% Aqueous Solution of Gd-5: 1500 g	"

Table 25

Sample	Reticulation	
	Processing No. 10	Processing No. 11
9a	A	B
9b	B	C
9c	D	E
9d	A	A
9e	A	A

Table 26

Sample	Relative Sensitivity (taking 9c as 100)			Fog Determined by Subtracting Fog due to Colored Coupler		
	RL	GL	BL	RL	GL	BL
9a	79	85	89	0.18	0.21	0.23
9b	85	92	96	0.15	0.17	0.19
9c	100	100	100	0.10	0.11	0.14
9d	98	100	105	0.11	0.11	0.13
9e	100	102	105	0.10	0.12	0.14

The above-described results were obtained by measuring those processed according to Processing No. 10. (Since Processing No. 11 was the same as Processing No. 10 except for the high temperature, the results with Processing 11 cannot be used to compare the photographic properties, although the results can be used for comparing reticulation.)

From the results given in Table 25, it can be seen that a great amount of a hardener enables the formation of a film in which reticulation does not occur in processing at 38°C without a hardening step, even when the gelation derivative is not used. However, as can be seen from Table 26, great side effects result in that the sensitivity is reduced because the film becomes so hardened that swelling is very much depressed, and in that fog increases due to the use of a large amount of hardener which (tends to cause fog). On the other hand, with samples using the gelation derivative in the uppermost layer, since a large amount of hardener is not required, neither a reduction in sensitivity nor an increase in fog was observed. On the contrary, the sensitivity of BL favorably increases due to the increase in swelling of the protective layer. From this standpoint too, it can seen that the use of the gelation derivative in the uppermost layer markedly improves the processability of lightsensitive materials in rapid processing at an elevated temperature.

EXAMPLE 10

The degrees of reticulation upon processing the same samples as described in Example 1 according to Processing No. 4 are shown in Table 27.

Table 27

Sample	Reticulation
1a	E (Partly delaminated)
1b	E
1c	A
1d	B
1e	C

From the results given in Table 27, it can be seen that, even when the processing was conducted at a temperature as high as 65°C, it is possible to form a reticulation-free film by using the gelation derivative.

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.

What is claimed is:

1. A method for rapidly forming photographic images, which comprises first image-wise exposing and then development of a photographic light-sensitive material which includes a support having thereon at least one silver halide emulsion layer and an uppermost layer containing a gelatin derivative, at a temperature of at least 30°C, said gelatin derivative being the reaction product of gelatin with a monofunctional compound selected from an isocyanate, an aziridine and a sulfonyl halide, and said gelatin derivative being present in an amount of not less than 20% by weight based on the total weight of said uppermost layer.

2. The method of claim **1**, wherein said gelatin is alkali-processed gelatin, acid-processed gelatin, enzyme-processed gelatin, hydrolyzed products of said alkali-processed, acid-processed or enzyme processed gelatin, or synthetic gelatin.

3. A method of claim **1**, wherein said isocyanate is phenyl isocyanate, p-tolyl isocyanate, 4-bromophenyl isocyanate, 4-chlorophenyl isocyanate, 2-nitrophenyl isocyanate, 4-ethoxycarbonylphenyl isocyanate, 1-naphthyl isocyanate, phenyl isocyanate bisulfite adduct, or a precursor thereof.

4. A method of claim **1**, wherein said aziridine is N-pentanoyl-2-ethyl-1-aziridine, 1-phenylcarbamoylaziridine, 2-methyl-1-phenylcarbamoylaziridine, 1-dimethylaminosulfonyl-aziridine, 1-benzoylaziridine, 4-nitrobenzyol-1-aziridine, 1-(2-chloro-phenyl)carbamoyl-1-aziridine, 1-(3-methylphenyl)carbamoylaziridine, 1-(n-butylsulfonyl)aziridine, 1-(phenylsulfonyl)-2-methylaziridine, 2-(1-aziridinyl-4,6-bisethylamino 1,3,5-triazine, 1-phenyl-3-(2-chloroethyl)-urea, or a precursor thereof.

5. The method of claim **1**, wherein said sulfonyl halide is benzenesulfonyl chloride, 4-methoxybenzene-sulfonyl chloride, 4-phenoxybenzenesulfonyl chloride, 4-chlorobenzene-sulfonyl chloride, 4-bromobenzene-sulfonyl chloride, 4-methylbenzenesulfonyl chloride, 3-nitrobenzenesulfonyl chloride, 3-carboxybenzenesulfonyl chloride, 2-naphthalenesulfonyl chloride, 4-aminobenzenesulfonyl fluoride, 3,4-diaminobenzenesulfonyl fluoride, 3-carboxybenzenesulfonyl fluoride, methane-sulfonyl chloride or ethane-sulfonyl chloride.

6. The method of claim **1**, wherein said monofunctional compound is phenyl isocyanate, p-tolyl isocyanate, 1-phenylcarbamoylaziridine, 2-methyl-1-phenylcarbamoylaziridine, 1-dimethylaminosulfonylaziridine, 1-benzoylaziridine, benzenesulfonyl chloride, 4-methoxybenzenesulfonyl chloride, 4-chlorobenzenesulfonyl chloride, 4-bromobenzenesulfonyl chloride, or 4-methylbenzenesulfonyl chloride.

7. The method of claim **1**, wherein said uppermost layer consists of a gelatin derivative.

8. The method of claim **1**, wherein said uppermost layer comprises a mixture of said gelatin derivative and at least one other hydrophilic binder.

9. The method of claim **8**, wherein said hydrophilic binder is a natural high molecular weight compound or a synthetic polymer.

10. The method of claim **9**, wherein said high molecular weight substance is non-modified gelatin, albumin, casein, agar-agar, sodium alginate, water soluble starch, a carboxy cellulose alkyl eater, hydroxyethyl cellulose, carboxymethyl hydroxyethyl cellulose, polyvinyl alcohol, partially esterified polyvinyl alcohol, polyacrylamide or a derivative thereof polyvinyl pyrrolidone, polyacrylic acid or a copolymer thereof, an acrylate, or a copolymer thereof, or a copolymer of maleic anhydride and another vinyl compound.

11. The method of claim **1**, wherein said uppermost layer includes at least one of a hardener, a matting agent, or a lubricant.

12. The method of claim **11**, wherein said hardener is an aldehyde, a formaldehyde precursor containing a methylol group of an alkylaminomethyl group, a [illegible] dioxane, an aziridine, an isoxazole, a carbodiimide, an active halogen containing compound, or an active vinyl compound.

13. The method of claim **11**, wherein said matting agent is silver halide grains, strontium barium sulfate or a water-dispersable vinyl polymer.

14. The method of claim **11**, wherein said lubricant is a liquid paraffin, a higher fatty acid ester, a polyfluorinated hydrocarbon or a silicone.

15. The method of claim **1**, wherein said development comprises black-and-white development.

16. The method of claim **1**, wherein said development comprises color development.

17. The method of claim **1**, wherein said photographic light-sensitive material is a color negative film, a color reversal film containing a coupler in the emulsion, a color positive film, a color paper, a coupler-[illegible] reversal color film or a black and white film.

18. The method of claim **1**, wherein said photographic light-sensitive material is a multi-layer sensitive material comprising a support having thereon in order from the support a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, a blue-sensitive silver halide emulsion layer and said uppermost layer containing said gelatin derivative.

19. The method of claim **1**, wherein said photographic light-sensitive material is a multi-layer light-sensitive material comprising a support having thereon in order from the support a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, a red-sensitive emulsion layer and said uppermost layer containing said gelatin derivative with the order of the green-sensitive layer and the red-sensitive layer being optional.

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