

[54] **PHOTOGRAPHIC PRODUCTS AND
PROCESSES WITH SILVER COMPLEXES
AS ANTIFOGGANTS**

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G03c 1/08

[58] **Field of Search**..... **96/3, 29 D, 29 R, 76 R,**
96/77, 95, 74, 110, 63

[56]

References Cited

UNITED STATES PATENTS

3,178,285	4/1965	Anderau et al.	96/99
3,552,968	1/1971	Willems	96/76 R
3,615,428	10/1971	Weed	96/29 R
3,647,437	3/1972	Land	96/3

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[57]

ABSTRACT

Compounds represented by the formula $\text{Ag}(\text{L})^{+2} 2\text{X}^{-}$, wherein L is a macrocyclic ligand and X is an anion, are used for the prevention of fog in photographic products and processes, particularly diffusion transfer products and processes.

28 Claims, No Drawings

PHOTOGRAPHIC PRODUCTS AND PROCESSES WITH SILVER COMPLEXES AS ANTIFOGGANTS

The present invention relates to photography and more particularly to photographic products and processes.

It has been extensively reported in literature pertaining to photography that photosensitive silver halide emulsions, and particularly photosensitive gelatino-silver halide emulsions, have a tendency to lose sensitivity and to become spontaneously developable without exposure to light. This phenomenon, characterized as "chemical fog," may be defined as the density above base level that is developed in emulsion areas that have received no intentional exposure and, in general, is not uniformly distributed over a selectively photoexposed emulsion, being greatest in the unexposed areas and decreasing with increased exposure in a non-linear manner.

In both silver and color photographic systems, the latter where silver halides are used to control image dye formation, fog results in a loss of image acuity.

Chemical fog may be divided into two classes: inherent fog, that is, fog which is emulsion initiated; and induced fog, that is, fog which is initiated during development. Induced fog appears to be due to physical development about extra-granular centers and inherent fog is probably due to the presence of grains bearing a catalytic site sensitivity speck which is unavoidably introduced and which is equivalent in its properties to latent image. Induced fog accordingly may be unaffected by the level of inherent fog. Thus it will be readily appreciated that an emulsion susceptible to the development of chemical fog requires silver halide grains possessing a catalytic center of sufficient size to be spontaneously developable and/or grains unprotected from non-discriminatory development.

Various and sundry procedures and additives have been disclosed in the art to provide an increase in the stability of photosensitive silver halide emulsions by reducing the tendency of photosensitive compositions to fog. These procedures usually increase the speed-to-fog ratio; otherwise there would be no point in using them unless the requirement for a low fog level completely overrides that for sensitivity. In general, the methods available for the control of fog are to increase the bromide ion concentration during the emulsion fabrication process; select "fog free" gelatins, i.e., gelatins which are free of fogging contaminants and which have desirable ratios of restrainer to sensitizer; reduce the level of chemical sensitization; and add inorganic or organic fog retarding adjuncts.

This invention relates primarily to the latter item above, and more particularly, to the use of a specified class of antifoggants.

Various diffusion transfer systems for forming color images have heretofore been disclosed in the art. Generally speaking, such systems rely for color image formation upon a differential in mobility or solubility of a dye image-providing material obtained as a function of development so as to provide an imagewise distribution of such material which is more diffusible and which is therefore selectively transferred, at least in part, by diffusion, to a superposed dyeable stratum to impart thereto the desired color transfer image. The differential in mobility or solubility may for example be ob-

tained by a chemical action such as a redox reaction or a coupling reaction.

The dye image-providing materials which may be employed in such processes generally may be characterized as either (1) initially soluble or diffusible in the processing composition but are selectively rendered non-diffusible in an imagewise pattern as a function of development; or (2) initially insoluble or non-diffusible in the processing composition but which are selectively rendered diffusible in an imagewise pattern as a function of development. These materials may be complete dyes or dye intermediates, e.g., color couplers.

As examples of initially soluble or diffusible materials and their application in color diffusion transfer, mention may be made of those disclosed, for example, in U.S. Pat. Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,802,735; 2,774,668; and 2,983,606. As examples of initially non-diffusible materials and their use in color transfer systems, mention may be made of the materials and systems disclosed in U.S. Pat. Nos. 3,443,939; 3,443,940; 3,227,550; 3,227,551; 3,227,552; 3,227,554; 3,243,294 and 3,445,228.

In any of these systems, multicolor images are obtained by employing a film unit containing at least two selectively sensitized silver halide layers each having associated therewith a dye image-providing material exhibiting desired spectral absorption characteristics. The most commonly employed elements of this type are the so-called tripack structures employing a blue-, a green, and a red-sensitive silver halide layer having associated therewith, respectively, a yellow, a magenta and a cyan dye image-providing material.

A particularly useful system for forming color images by diffusion transfer is that described in U.S. Pat. No. 2,983,606, employing dye developers (dyes which are also silver halide developing agents) as the dye image-providing materials. In such systems, a photosensitive element comprising at least one silver halide layer having a dye developer associated therewith (in the same or in an adjacent layer) is developed by applying an aqueous alkaline processing composition. Exposed and developable silver halide is developed by the dye developer which in turn becomes oxidized to provide an oxidation product which is appreciably less diffusible than the unreacted dye developer, thereby providing an imagewise distribution of diffusible dye developer in terms of unexposed areas of the silver halide layer, which imagewise distribution is then transferred, at least in part, by diffusion, to a dyeable stratum to impart thereto a positive dye transfer image. Multicolor images may be obtained with a photosensitive element having two or more selectively sensitized silver halide layers and associated dye developers, a tripack structure of the type described above and in various patents including the aforementioned U.S. Pat. No. 2,983,606 being especially suitable for accurate color recordation of the original subject matter.

In color diffusion transfer systems of the foregoing description, color images are obtained by exposing a photosensitive element or "negative component" comprising at least a light-sensitive layer, e.g., a gelatino silver halide emulsion layer, having a dye image-providing material associated therewith in the same or in an adjacent layer, to form a developable image; developing this exposed element with a processing composition to form an imagewise distribution of a soluble and diffusible image-providing material; and transfer-

ring this imagewise distribution, at least in part, by diffusion, to a superposed receiving element or "positive component" comprising at least a dyeable stratum to impart to this stratum a color transfer image. The negative and positive components may be separate elements which are brought together during processing and thereafter either retained together as the final print or separated following image formation; or they may together comprise a unitary structure, e.g., integral negative-positive film units wherein the negative and positive components are laminated and/or otherwise physically retained together at least prior to image formation.

While the present invention is applicable both to those systems wherein the dyeable stratum is contained on a separate element and to those systems wherein the dyeable stratum and the photosensitive strata comprise a unitary structure, of particular interest are those integral negative-positive film units adapted for forming color transfer images viewable without separation, i.e., wherein the positive component need not be separated from the negative component for viewing purposes. Generally, such film units comprise a plurality of essential layers including a negative component comprising at least one light-sensitive silver halide and associated dye image-providing material and a positive component comprising dyeable stratum. These components may be laminated together or otherwise secured together in physical juxtaposition as a single structure. Film units intended to provide multicolor images comprise two or more selectively sensitized silver halide layers each having associated therewith an appropriate dye image-providing material exhibiting desired spectral absorption characteristics. As was heretofore mentioned the most commonly employed negative components for forming multicolor images are of the tripack structure containing a blue-, a green- and a red-sensitive silver halide layer having associated therewith in the same or in a contiguous layer a yellow, a magenta and a cyan dye image-providing material respectively. Interlayers or spacer layers may if desired be provided between the respective silver halide layers and associated dye image-providing materials. In addition to the aforementioned essential layers, such film units further include means for providing a reflecting layer between the dyeable stratum and the negative component in order to mask effectively the silver image or images formed as a function of development of the silver halide layer or layers and any remaining associated dye image-providing material and to provide a background for viewing the color image formed in the dyeable stratum, without separation, by reflected light. This reflecting layer may comprise a preformed layer of a reflecting agent included in the essential layers of the film unit or the reflecting agent may be provided after photoexposure, e.g., by including the reflecting agent in the processing composition. These essential layers are preferably contained on a transparent dimensionally stable layer or support member positioned closest to the dyeable stratum so that the resulting transfer image is viewable through this transparent layer. Most preferably another dimensionally stable layer which may be transparent or opaque is positioned on the opposed surface of the essential layers so that the aforementioned essential layers are sandwiched or confined between a pair of dimensionally stable layers or support members, at least one of which is transparent to permit viewing

therethrough of a color transfer image obtained as a function of development of the exposed film unit in accordance with the known color diffusion transfer system such as will be detailed hereinafter. In a particularly preferred form such film units are employed in conjunction with a rupturable container of known description containing the requisite processing composition and adapted upon application of pressure of applying its contents to develop the exposed film unit, e.g., by applying the processing composition in a substantially uniform layer between the dyeable stratum and the negative component. It will be appreciated that the film unit may optionally contain other layers performing specific desired functions, e.g., spacer layers, etc.

Opacifying means may be provided on either side of the negative component so that the film unit may be processed in the light to provide the desired color transfer image. In a particularly useful embodiment such opacifying means comprise an opaque dimensionally stable layer or support member positioned on the free or outer surface of the negative component, i.e., on the surface of the film unit opposed from the positive component containing the dyeable stratum to prevent photo-exposure by actinic light incident thereon from this side of the film unit and an opacifying agent applied during development between the dyeable stratum and the negative component, e.g., by including the opacifying agent in a developing composition so applied, in order to prevent further exposure (fogging) by actinic light incident thereon from the other side of the film unit when the thus exposed film unit is developed in the light. The last-mentioned opacifying agent may comprise the aforementioned reflecting agent which masks the negative component and provides the requisite background for viewing the transfer image formed thereover. Where this reflecting agent does not by itself provide the requisite opacity it may be employed in combination with an additional opacifying agent in order to prevent further exposure of the light-sensitive silver halide layer or layers by actinic light incident thereon.

As examples of such integral negative-positive film units for preparing color transfer images viewable without separation as reflection prints, mention may be made of those described and claimed in U.S. Pat. Nos. 3,415,644; 3,415,645; 3,415,646; 3,473,925; 3,573,043; 3,576,625; 3,573,042; 3,594,164; and 3,594,165.

In general, the integral negative-positive film units of the foregoing description, e.g., those described in the aforementioned patents, are exposed to form a developable image and thereafter developed by applying the appropriate processing composition to develop exposed silver halide and to form, as a function of development, an imagewise distribution of diffusible dye image-providing material which is transferred, at least in part by diffusion, to the dyeable stratum to impart thereto the desired color transfer image, e.g., a positive color transfer image. Common to all of these systems is the provision of a reflecting layer between the dyeable stratum and the photosensitive strata to mask effectively the latter and to provide a background for viewing the color image contained in the dyeable stratum, whereby this image is viewable without separation, from the other layers or elements of the film unit. In certain of these systems, this reflecting layer is provided prior to photoexposure, e.g., as a preformed layer

included in the essential layers of the laminar structure comprising the film unit, and in others it is provided at some time thereafter, e.g., by including a suitable light-reflecting agent, for example, a white pigment such as titanium dioxide, in the processing composition which is applied between the dyeable stratum and the next adjacent layer to develop the latent image and to form the color transfer image.

A preferred opacification system to be contained in the processing composition is that described in the copending application of Edwin H. Land, Ser. No. 43,782, filed June 5, 1970 and U.S. Pat. No. 3,647,437 issued Mar. 7, 1972, which are incorporated herein by reference in their entirety.

In lieu of having the reflecting pigment contained in the processing composition, the reflecting pigment needed to mask the photosensitive strata and to provide the requisite background for viewing the color transfer image formed in the receiving layer may be contained initially in whole or in part as a preformed layer in the film unit, as that disclosed in the U.S. Pats. of Edwin H. Land, Nos. 3,615,421 issued Oct. 26, 1972 and 3,620,724 issued Nov. 16, 1971. The reflecting pigment may be generated in situ as is disclosed in the U.S. Pats. of Edwin H. Land, Nos. 3,647,434 and 3,647,435, both issued Mar. 7, 1972.

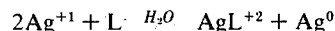
In the various color diffusion transfer systems which have previously been described and which employ an aqueous alkaline processing fluid, it is well known to employ an acid-containing layer to lower the environmental pH following substantial dye transfer in order to increase the image stability and/or to adjust the pH from a first pH at which the imaging dyes are diffusible to a second (lower) pH at which they are not. For example, U.S. Pat. No. 3,362,819 discloses systems wherein the desired pH reduction may be effected by providing a polymeric acid layer adjacent the dyeable stratum. As examples of other useful neutralizing layers, in addition to those disclosed in the aforementioned U.S. Pat. No. 3,362,819, mention may be made of those disclosed in the following copending applications: Ser. No. 165,171 of Schlein et al., filed July 22, 1971; Ser. No. 214,746 of Bedell, filed Jan. 3, 1972; Ser. No. 208,616 of Taylor, filed Dec. 16, 1971; Ser. No. 231,835 (Case No. 4526) of Sahatjian et al., filed Mar. 6, 1972, etc.

An inert interlayer or spacer layer may be and is preferably disposed between the polymeric acid layer and the dyeable stratum in order to control the pH reduction so that it is not premature and hence interferes with the development process, e.g., to "time" control the pH reduction. Suitable spacer or "timer" layers for this purpose are described with particularity in U.S. Pat. No. 3,362,819 and in others, including U.S. Pat. Nos. 3,419,389; 3,421,893; 3,433,633; 3,455,686; and 3,575,701.

While the acid layer and associated spacer layer are preferably contained in the receiving element employed in systems wherein the dyeable stratum and photosensitive strata are contained on separate elements, e.g., between the support for the receiving element and the dyeable stratum; or associated with the dyeable stratum in those integral film units, e.g., on the side of the dyeable stratum opposed from the negative component, they may, if desired, be associated with the photosensitive strata, as is disclosed, for example, in U.S. Pat. Nos. 3,362,821 and 3,573,043. In film units

such as those described in the aforementioned U.S. Pat. Nos. 3,594,164 and 3,594,165, they also may be contained on the spreader sheet employed to facilitate application of the processing fluid.

Copending application Ser. No. 327,797, filed Jan. 29, 1973, now abandoned and replaced by continuation-in-part application Ser. No. 475,778, filed June 3, 1974, discloses the disproportionation of Ag^{+1} in the vicinity of the latent image by associating the silver halide emulsion layer with a macrocyclic ligand which is described in detail in the indicated application and which will be described below. It is believed that the reaction proceeds as follows:

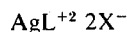


wherein L is the ligand. Disposal of the ligand L in the emulsion acts as a sensitization or latensification agent.

By employing compounds containing the described ligands superior antifoggant properties can be achieved.

SUMMARY OF THE INVENTION

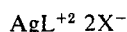
A compound which is water-soluble and stable in aqueous medium represented by the formula:



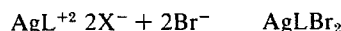
wherein L is a macrocyclic ligand and X is an anion, has been found to provide superior antifoggant activity when disposed in a silver halide emulsion.

DETAILED DESCRIPTION OF THE INVENTION

It has now been found that superior antifoggant properties have been achieved by disposing in a silver halide emulsion a water-soluble Ag^{+2} salt of the formula:

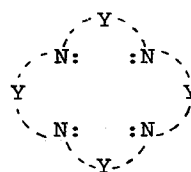


wherein L is a macrocyclic ligand and X is an anion. While not intending to be bound by theory, it is believed that the water-soluble, stable Ag^{+2} salts react with bromine ions in the vicinity of the grain precipitating on the grain according to the following equation:



The Ag^{+2} salts are electron deficient, i.e., electron sinks, thus they are fog sinks and will destroy fog centers on the grain.

The ligand L employed in the present invention is a macrocyclic ligand, i.e., long and flat, capable of stabilizing the Ag^{+2} ion and which possesses four electron donor atoms, preferably containing four atoms capable of providing the described stabilizing effect to silver. Thus, the ligands suitable for use in the present invention may be represented by the formulae:



A.

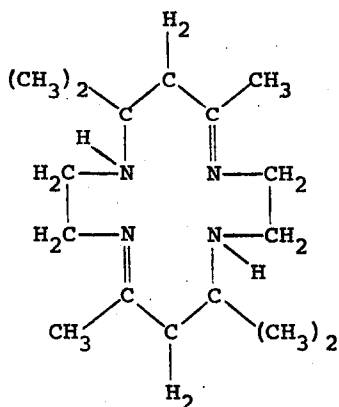
wherein each Y comprises the atoms linking the respective nitrogen atoms and which, together with the respective nitrogen atoms, constitute the ring system.

Preferably, the ligand comprises saturated and unsaturated macrocyclic Schiff base amines.

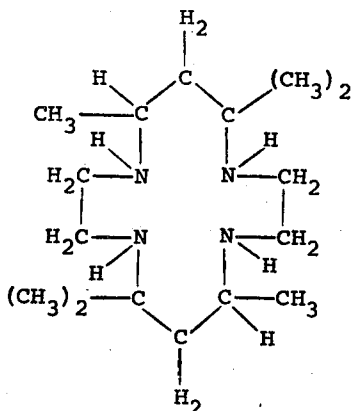
7

As examples of suitable ligands, mention may be made of the following:

A.

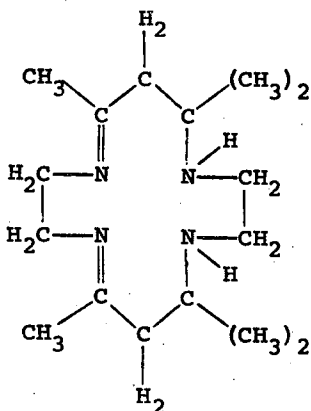


B.



5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (teta)

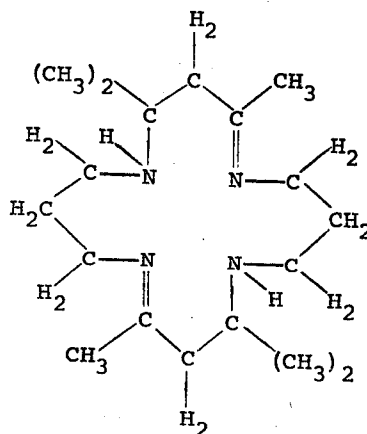
C.



8

5

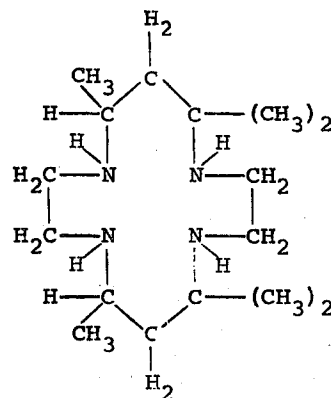
D.



20

25

E.



35

5,5,7,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet b)

The preparation of such ligands is known to the art. See, for example, J.A.C.S. 2644 (1964).

45

50 The preparation of such ligands is known to the art. See, for example, J.A.C.S. 2644 (1964).

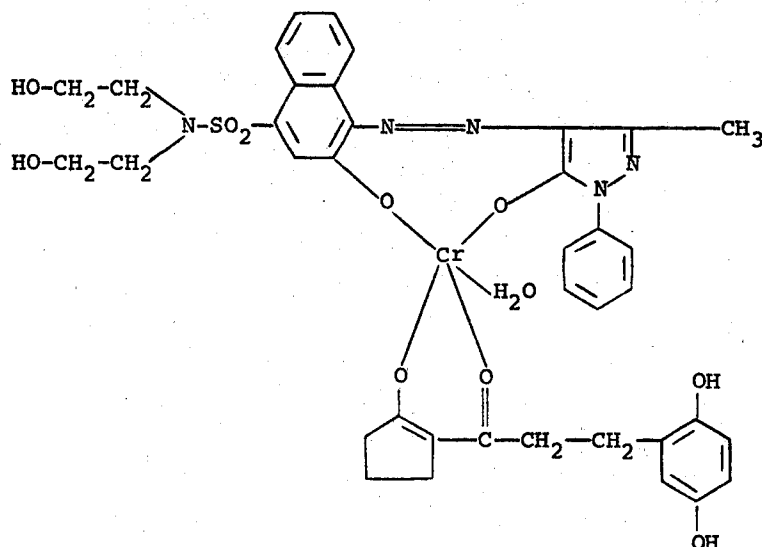
55 The anion designated X may constitute any inorganic or organic anion imparting water-solubility to the salt and which is photographically innocuous when disposed in the emulsion. As examples of suitable anions, mention may be made of NO_3^- , ClO_4^- , $\frac{1}{2} \text{SO}_4^{2-}$, Br^- and CH_3CO_2^- .

60 The Ag^{+2} salt is disposed in the silver halide emulsion and is generally employed at a level of about 0.20 mgs./ft.² to 0.50 mgs./ft.².

65 The following nonlimiting examples illustrate the novel emulsions of the present invention. The Controls indicated in each Example differed from the invention only in the absence of the silver salt.

EXAMPLE I

A film unit was prepared by coating a polyester support with 50 mgs./ft.² of magenta dye developer of the formula:



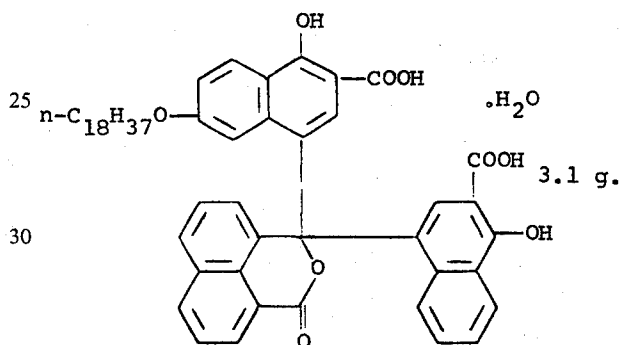
in about 150 mgs./ft.² of gelatin. Over the above-described layer was coated a blue-sensitized silver iodobromide emulsion containing 0.32 mgs./ft.² of Ag(-teta)⁺ 2NO₃⁻ at a coverage of about 80 mgs./ft.² of silver and about 80 mgs./ft.² of gelatin. Over the emulsion layer was coated a layer of gelatin at a coverage of about 30 mgs./ft.² containing about 8 mgs./ft.² of 4'-methylphenylhydroquinone. The thus-formed negative was exposed through a step wedge to selectively filtered radiation and then processed by contacting the negative with a processing composition while in superposition with an image-receiving element in the dark for 10 minutes. The image-receiving element comprised a 4 mil polyethylene terephthalate film base having coated thereon the following layers:

1. the partial butyl ester of polyethylene/maleic anhydride copolymer prepared by refluxing, for 14 hours, 300 grams of high viscosity poly-(ethylene/maleic anhydride), 140 grams of n-butyl alcohol and 1 cc. of 85 percent phosphoric acid to provide a polymeric acid layer approximately 0.75 mil thick;

2. a 10 percent aqueous emulsion of a diacetone acrylamide/acrylamide copolymer grafted onto a polyvinyl alcohol backbone to provide an inert spacer layer approximately 0.3 mil thick; and

3. A 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, at a coverage of approximately 600 mgs./ft.², to provide a polymeric image-receiving layer approximately 0.40 mil thick. The processing composition comprised the following:

Potassium hydroxide (85%)	5.3	g.
N-benzyl- α -picolinium bromide (50% solution in water)	1.3	g.
N-phenethyl- α -picolinium bromide	0.775	g.
Sodium carboxymethyl cellulose (Hercules Type 7H4F providing a viscosity of 3000 cps. at 1% in water at 25°C.)	0.59	g.
Titanium dioxide	44.9	g.
6-methyl uracil	0.63	g.
bis-(β -aminoethyl)-sulfide	0.045	g.
Lithium nitrate	0.1	g.
Benzotriazole	0.6	g.
6-methyl-5-bromo-4-azabenzimidazole	0.03	g.
Colloidal silica aqueous dispersion (30% SiO ₂)	1.96	g.
Lithium hydroxide	0.2	g.
6-benzylamino-purine	0.42	g.
Polyethylene glycol (M.W. 6000) Water	0.58	cc



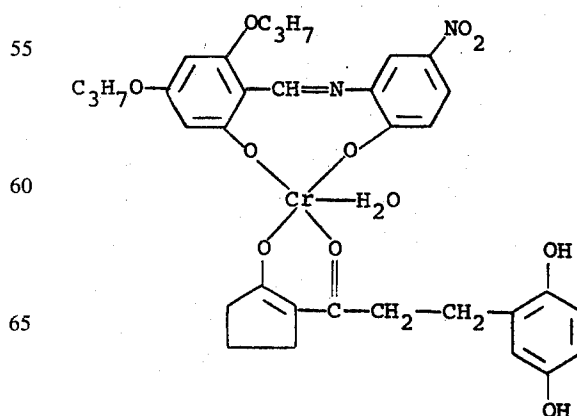
The film unit of the present invention, compared with a film unit prepared and processed as above except that no silver salt was disposed therein, showed the following positive dye D_{max} :

D_{max} Control	1.85
D_{max} Test	2.03

The significant increase in positive D_{max} is evidence of the suppression of fog in the emulsion of the present invention.

EXAMPLE II

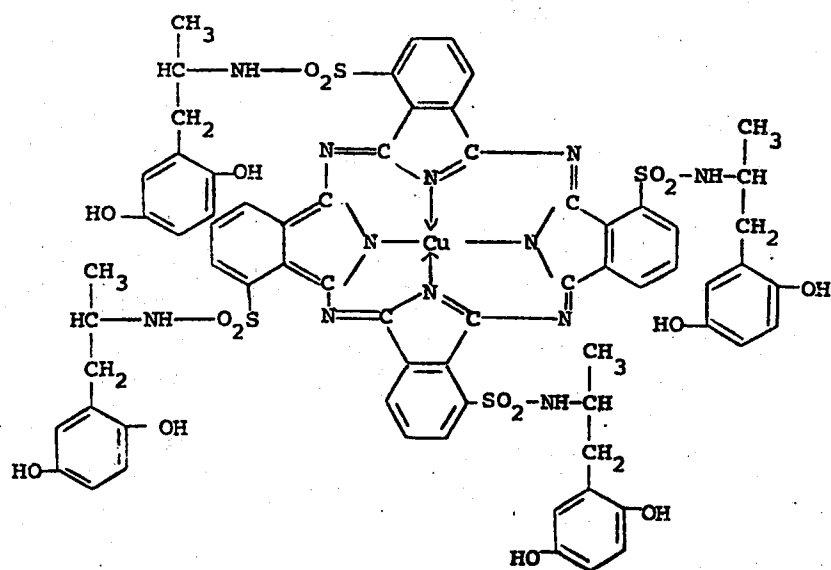
A film unit was prepared by coating a polyester support with 50 mgs./ft.² of yellow dye developer of the formula:



in about 75 mgs./ft.² of gelatin. Over the above-described layer was coated a blue-sensitized silver iodobromide emulsion containing 0.32 mgs./ft.² of Ag(-teta)⁺² 2NO₃⁻ at a coverage of about 80 mgs./ft.² of silver and about 80 mgs./ft.² of gelatin. Over the emulsion layer was coated a layer of gelatin at a coverage of about 30 mgs./ft.² containing about 8 mgs./ft.² of 4'-methylphenylhydroquinone. The thus-formed negative was exposed and processed as in Example I. The image-receiving element and processing composition employed were the same as those used in Example I. D_{max} Control 1.15, D_{max} Test 1.40.

EXAMPLE III

A film unit was prepared by coating a polyester support with 50 mgs./ft.² of cyan dye developer of the formula:

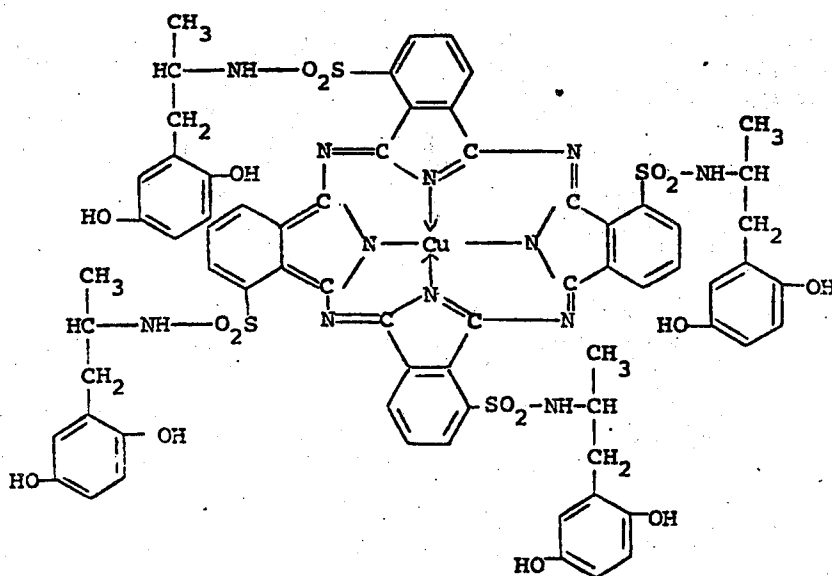


in about 75 mgs./ft.² of gelatin. Over the above-described layer was coated a red-sensitized silver iodobromide emulsion containing 0.32 mgs./ft.² of Ag(-teta)⁺² 2NO₃⁻ at a coverage of about 80 mgs./ft.² of silver and about 80 mgs./ft.² of gelatin. Over the emulsion layer was coated a layer of gelatin at a coverage of about 30 mgs./ft.². The thus-formed negative was exposed and processed as in Example I above.

D _{max} Control	1.85
D _{max} Test	2.15

EXAMPLE IV

A film unit was prepared by coating a polyester support with 50 mgs./ft.² of cyan dye developer of the formula:

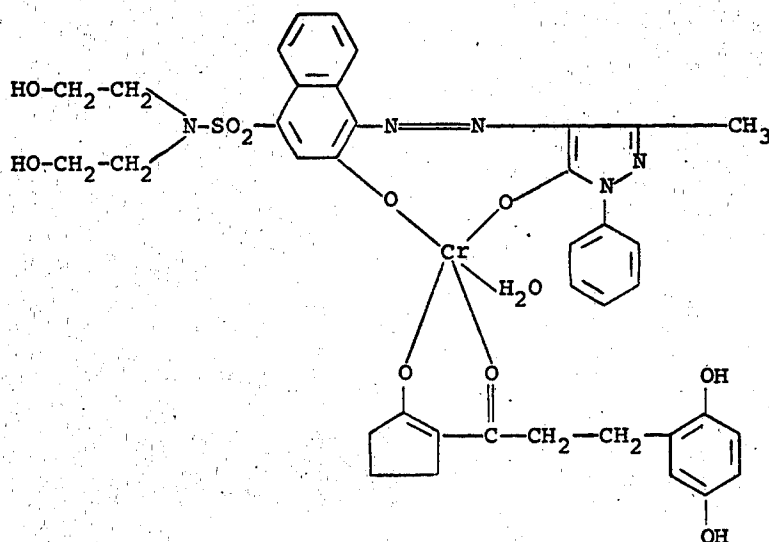


in about 75 mgs./ft.² of gelatin. Over the above-described layer was coated a red-sensitized silver iodobromide emulsion containing 0.32 mgs./ft.² of Ag(-teta)⁺² 2NO₃⁻ at a coverage of about 80 mgs./ft.² of silver and about 80 mgs./ft.² of gelatin. Over the emulsion layer was coated a layer of gelatin at a coverage of about 30 mgs./ft.² containing about 8 mgs./ft.² of 4'-methylphenylhydroquinone. The thus-formed negative was exposed and processed as in Example I above.

D_{max} Control	1.73
D_{max} Test	2.17

EXAMPLE V

A film unit was prepared by coating a polyester support with 50 mgs./ft.² of a magenta dye developer of the formula:



in about 75 mgs./ft.² of gelatin. Over the above-described layer was coated a green-sensitized silver iodobromide emulsion containing 0.32 mgs./ft.² of Ag(-teta)⁺² 2NO₃⁻ at a coverage of about 80 mgs./ft.² of silver and about 80 mgs./ft.² of gelatin. Over the emulsion was coated a layer of gelatin at a coverage of about 30 mgs./ft.². The thus-formed negative was exposed and processed as in Example I above except that the processing composition additionally contained 0.2 percent of 4'-methylphenylhydroquinone.

D_{max} Control	1.96
D_{max} Test	2.15

By employing the novel silver halide emulsions of the present invention, it will be noted that less fog is produced than with similar emulsions which do not contain the novel antifoggant of the present invention.

While the invention has been defined primarily with regard to photographic systems employing dye developers, it should be understood the silver halide emul-

sions of the present invention are suitable for use in photographic systems employing other dye image-forming materials as described in the above-mentioned patents and applications. The silver halide emulsions of the present invention also find particular utility in black and white photographic processes and, particularly, in panchromatically sensitized silver halide emulsions employed in additive color photography.

EXAMPLE VI

A film unit was prepared by coating a polyester support with 150 mgs./ft.² of a blue-sensitive silver iodobromide emulsion containing 6 mg./g. of silver of Ag(-teta)⁺² 2ClO₄. The emulsion layer was overcoated with 30 mgs./ft.² of gelatin. The thus-formed negative was exposed according to the procedure of Example I. The processing composition and image-receiving element employed were from a Polaroid Type 107 film unit (Polaroid Corporation, Cambridge, Massachusetts). The thus-formed negative, as compared with a film unit pre-

pared and processed above, except that it contained no silver salt, showed the following positive silver density:

D_{max} Control	1.56
D_{max} Test	1.78

In all of the above experiments the D_{min} was substantially the same for the control and test negatives.

A preferred film unit employs an image-receiving component intermediate the photosensitive silver halide stratum and the additive multicolor screen. In such a film unit, exposure of the silver halide emulsion is accomplished through the screen unit and the image-receiving component. Subsequent processing results in the formation of a positive silver image in the image-receiving component next adjacent the additive multicolor screen. The aforementioned film unit is one example of a structure which obviates registration problems since the screen employed for exposing is in automatic registration with the positive silver image for viewing. In the aforementioned film unit, the silver halide stratum may be removed or allowed to remain in position subsequent to formation of the positive silver image.

As examples of suitable film structures which comprise negative and positive images in superposition and formed by diffusion transfer reversal processes, mention may be made of U.S. Pat. Nos. 2,861,885; 2,726,154; 2,944,894; 3,536,488; and also U.S. Pat. Nos. 3,615,427; 3,615,428; 3,615,429 and 3,615,426.

The utility of such film units wherein the silver halide layer remains an integral portion of the film unit subsequent to positive image formation is achieved by employing as the image-receiving element a layer which provides an unusually effective silver precipitating environment which causes the silver deposited therein to possess an extraordinarily high covering power in comparison with negative silver developed in the silver halide layer. For greater discussion of such a phenomena, see Edwin H. Land, *One Step Photography*, *Photographic Journal*, Section A, pages 7 to 15, January, 1950.

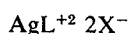
The above-mentioned integral film unit applications are particularly desirable for employment as cine film for motion picture projection, for example, such as the cine film system described in U.S. Pat. No. 3,615,427 issued Oct. 26, 1971. Processing of such film units, as well as the specific composition of the processing composition, is detailed in the aforementioned patents and applications.

The specific composition or method of preparation of silver halide emulsions suitable for use in the present invention is not critical to the operation of the present invention. For example, emulsions of the present invention may be employed in emulsions for wet processing, emulsions employed in diffusion transfer processing and direct positive emulsions. Conventional spectral and chemical sensitizers may be employed as well as optional additives such as coating aids, hardeners, viscosity increasing agents, stabilizers, preservatives, and the like.

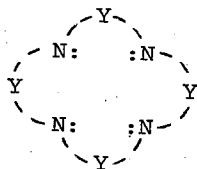
Similarly, the photoresponsive material will preferably comprise a crystal of a silver compound, for example, one or more of the silver halides such as silver chloride, silver iodide, silver bromide, or mixed silver halides such as silver chlorobromide, silver chloriodobromide, or silver iodobromide, of varying halide ratios and varying silver concentrations.

What is claimed is:

1. A photosensitive silver halide emulsion having associated therewith a stable, water-soluble compound of the formula:



wherein L is a non-aromatic macrocyclic ligand having four electron donor atoms and is represented by the formula:



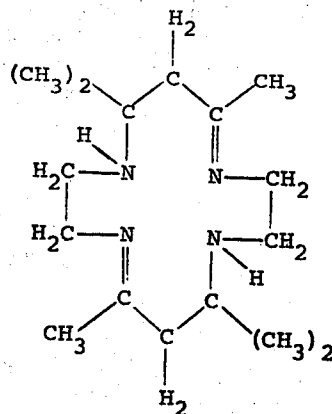
wherein each Y is a carbon chain of at least 2 carbon atoms and X is an anion.

2. A product as defined in claim 1 wherein said emulsion includes spectral sensitizing agents.

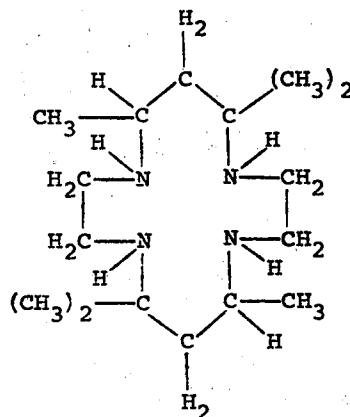
3. A product as defined in claim 1 wherein said emulsion includes chemical sensitizing agents.

4. The product as defined in claim 1 wherein L is a tetraamine.

5. The product as defined in claim 4 wherein L is

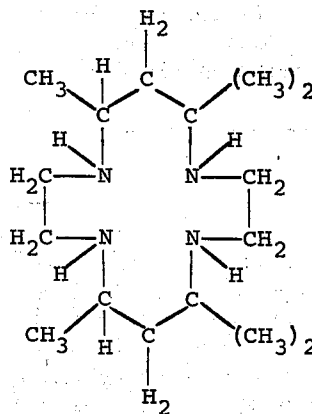


6. The product as defined in claim 4 wherein L is:



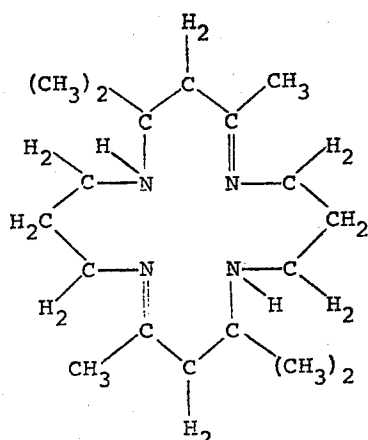
5,5,7,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane(teta).

7. The product as defined in claim 4, wherein L is:



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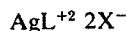
8. The product as defined in claim 4 wherein L is:



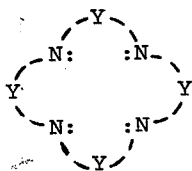
9. The product as defined in claim 1 wherein X is NO_3^- .

10. The product as defined in claim 1 wherein said silver halide emulsion is carried on a support.

11. A photographic silver diffusion transfer film unit which comprises photosensitive silver halide, silver precipitating nuclei and associated with said silver halide, a stable, water-soluble compound of the formula:



wherein L is a non-aromatic macrocyclic ligand having four electron donor atoms and is represented by the formula:



wherein each Y is a carbon chain of at least 2 carbon atoms and X is an anion.

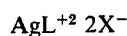
12. A product as defined in claim 11 wherein said film unit includes a common support carrying a layer comprising silver precipitating nuclei and a layer comprising silver halide crystals.

13. A product as defined in claim 12 wherein said film unit is a permanent laminate.

14. A product as defined in claim 12 wherein said common support is transparent.

15. A photographic silver diffusion transfer film unit as defined in claim 14 which includes an additive color screen intermediate said transparent common support and next adjacent essential layer.

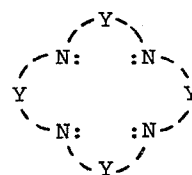
16. In a photosensitive element including at least one light-sensitive silver halide layer wherein each of which has a dye image-providing material associated therewith, the improvement which comprises including in at least one of said silver halide layers a stable, water-soluble compound of the formula:



wherein L is a non-aromatic macrocyclic ligand having

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four electron donor atoms and is represented by the formula:



wherein each Y is a carbon chain of at least 2 carbon atoms and X is an anion.

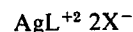
17. An element as defined in claim 16 which includes a red-sensitive gelatino silver halide emulsion having a cyan dye image-providing material associated therewith; a green-sensitive gelatino silver halide emulsion having a magenta dye image-providing material associated therewith; and a blue-sensitive gelatino silver halide emulsion having a yellow dye image-providing material associated therewith.

18. An element as defined in claim 16 which includes a positive component including at least a dyeable stratum.

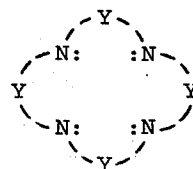
19. A photographic film unit which comprises, in combination:

a photosensitive element having a diffusion transfer image-receiving element affixed at least one edge thereof, said photosensitive element comprising a support carrying:

- a red-sensitive silver halide emulsion having associated therewith a cyan dye developer;
- a green-sensitive silver halide emulsion having associated therewith a magenta dye developer;
- a blue-sensitive silver halide emulsion having associated therewith a yellow dye developer; at least one of said silver halide emulsions having disposed therein a stable, water-soluble compound of the formula:



wherein L is a non-aromatic macrocyclic ligand having four electron donor atoms and is represented by the formula:



wherein each Y is a carbon chain of at least 2 carbon atoms and X is an anion;

said diffusion transfer image-receiving element comprising a support layer carrying:

an alkaline processing composition permeable and dyeable layer wherein said photosensitive and said image-receiving elements are adapted to be superposed, the support layers of each comprising the extremities of the superposed structure.

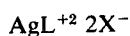
20. The product as defined in claim 19 wherein said compound is disposed in each of said silver halide emulsion layers.

21. The product as defined in claim 19 including a rupturable container retaining an aqueous alkaline processing composition affixed one edge of said photosensitive and said image-receiving elements and adapted upon rupture to distribute its contents intermediate said superposed photosensitive and said image-receiving elements.

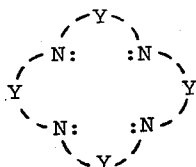
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22. The product as defined in claim 19 wherein said photographic film unit comprises a composite structure comprising said photosensitive element and said image-receiving element permanently affixed each to the other in superposed relationship, the support layers of each of said elements comprising the extremities of said composite structure.

23. A photographic process which comprises developing an exposed photosensitive element comprising an exposed silver halide emulsion containing a stable, water-soluble compound of the formula:



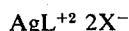
wherein L is a non-aromatic macrocyclic ligand having four electron donor atoms and is represented by the formula:



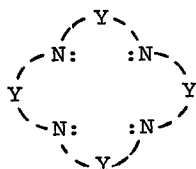
wherein each Y is a carbon chain of at least 2 carbon atoms and X is an anion.

24. A silver diffusion transfer photographic process which comprises, in combination, the steps of:

- a. exposing a photographic film unit comprising photosensitive silver halide and silver precipitating nuclei wherein said silver halide has associated therewith a stable, water-soluble compound of the formula:



wherein L is a non-aromatic macrocyclic ligand having four electron donor atoms and is represented by the formula:



wherein each Y is a carbon chain of at least 2 carbon atoms and X is an anion; and

- b. contacting said exposed film unit with a processing composition containing a silver halide developing agent and a silver halide solvent, thereby providing a visible diffusion transfer process silver image to said unit, as a function of the point-to-point degree of exposure thereof.

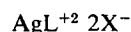
25. A diffusion transfer color photographic process as defined in claim 24 wherein said film unit includes a color screen and exposure of said film unit is accomplished by radiation transmitted through said screen.

26. A diffusion transfer multicolor photographic process as defined in claim 25 wherein said color screen comprises a trichromatic additive color screen comprising red, green and blue optical filter elements in a screen pattern.

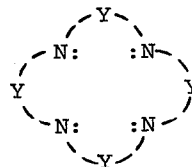
27. A silver diffusion transfer photographic process as defined in claim 25 which comprises, in combination, the steps of:

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- a. exposing a film unit which comprises a permanent laminate which includes a support carrying on one surface a layer comprising silver precipitating nuclei and a layer comprising photosensitive silver halide having associated therewith a stable, water-soluble compound of the formula:



wherein L is a non-aromatic macrocyclic ligand having four electron donor atoms and is represented by the formula:

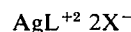


wherein each Y is a carbon chain of at least 2 carbon atoms and X is an anion; and

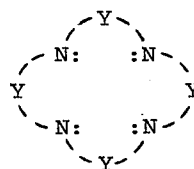
- b. contacting the exposed silver halide layer with an aqueous processing composition containing a silver halide developing agent and a silver halide solvent thereby providing a visible silver image to said film unit, in terms of the unexposed areas of said silver halide layer, as the function of the point-to-point degree of exposure thereof.

28. A process for forming photographic images which comprises, in combination, the steps of:

- a. exposing a photographic film unit which comprises a plurality of layers including at least a first photosensitive silver halide layer having associated therewith diffusion transfer dye image-providing material and a stable, water-soluble compound of the formula:



wherein L is a non-aromatic macrocyclic ligand having four electron donor atoms and is represented by the formula:



wherein each Y is a carbon chain of at least 2 carbon atoms and X is an anion, and a diffusion transfer process image-receiving layer adapted to receive solubilized image-forming material diffusing thereto;

- b. contacting said photosensitive silver halide emulsion with an aqueous alkaline processing composition;
- c. effecting thereby substantial development of said silver halide emulsion;
- d. forming thereby an imagewise distribution of mobile image-forming material as a function of the point-to-point degree of emulsion exposure; and
- e. transferring by diffusion at least a portion of said imagewise distribution of mobile image-forming material to said layer adapted to receive said material to provide thereto an image in terms of said imagewise distribution.

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