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3,748,138

METAL COMPLEX IN SILVER HALIDE DEVELOPMENT

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17 Claims

ABSTRACT OF THE DISCLOSURE

The rate of formation of metallic silver in the photographic process is increased by the use of a metal complex during photographic development.

This invention relates to photographic processes, and more particularly to photographic processes which increase the rate at which metallic silver is formed.

It is well known that exposed light-sensitive photographic silver halide grains can be converted to metallic silver images by photographic developing agents. It would be desirable if the rate of formation of silver images in the photographic process could be increased.

Christensen in U.S. Pat. 2,517,541, issued Aug. 8, 1950, describes photographic silver halide emulsions containing amounts less than about 0.1% by weight of the wet emulsion of an alkali metal cyanocobaltate. Tests indicate that the incorporation of alkali metal cyanocobaltate in such concentrations, or in concentrations 100 times greater than disclosed by Christensen, fail to effectively increase the rate of silver development.

It is one object of this invention to provide a process for developing metallic silver images in exposed light-sensitive silver halide grains.

A further object of this invention is to provide a process for increasing the rate of metallic silver development in the photographic process.

Other objects of this invention will be apparent from this disclosure and the appended claims.

In accordance with this invention, an improvement is provided in photographic processes in which exposed light-sensitive silver halide grains are developed to metallic silver with a photographic developing agent. The improvement in accordance with this invention comprises conducting the development in the presence of certain metal complexes which increase the rate at which metallic silver is formed.

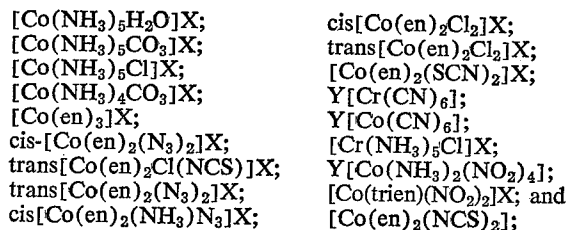
The metal complexes which are most useful in the practice of this invention are those which feature a molecule having a metallic atom or ion surrounded by a group of atoms, ions or other molecules which are generically referred to as ligands. The metallic atom or ion in the center of these complexes is a Lewis acid; the ligands are Lewis bases. Werner complexes are well known examples of such complexes. The useful metal salts are typically capable of existing in at least two valent states. In a preferred aspect of the invention, the metal complexes are those referred to by American chemists as "inert" and by European chemists as "robust." Particularly useful are complexes of a metal ion with a ligand which, when a test sample thereof is dissolved at .1 molar concentration at 20° C. in an inert solvent solution also containing .1 molar concentration of a tagged ligand of the same species which is uncoordinated, exhibits essentially no exchange of uncoordinated and coordinated ligands for at least one minute, and preferably for at least several hours, such as up to five hours or more. This test is advantageously conducted under the pH conditions which will be utilized in the practice of the invention, about 8 to 13. Many metal complexes useful in this invention show essentially no exchange of uncoordinated and coordinated

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ligands for several days. The definition of "inert" metal complexes, and the method of measuring ligand exchange using radioactive isotopes to tag ligands are well known in the art. See, for example, Taube, Chem. Rev., vol. 50, p. 69 (1952), and Basolo and Pearson, Mechanisms of Inorganic Reactions, a Study of Metal Complexes and Solutions, 2nd Edition, 1967, published by John Wiley and Sons, p. 141. Further details on measurement of ligand exchange appear in articles by Adamson et al., J. Am. Chem. Soc., vol. 73, p. 4789 (1951). The inert metal complexes should be contrasted with labile complexes which, when tested by the method described above, have a reaction half-life generally less than one minute. Metal chelates are a special type of metal complex in which the same ligand (or molecule) is attached to the central metal ion at two or more different points. The metal chelates generally exhibit somewhat slower ligand exchange than non-chelated complexes. Labile type chelates may have a half-life of several seconds, or perhaps slightly longer.

Preferred metal complexes in accordance with this invention have coordination numbers of 6, and are known as octahedral complexes. Most square planar complexes (which have coordination numbers of 4) are rather labile, although some Group VIII metal square planar complexes, particularly platinum and palladium square planar complexes, exhibit inertness to rapid ligand exchange. Cobalt and chromium metal complexes are especially useful in the practice of this invention. A wide variety of ligands can be used with a metal ion to form suitable metal complexes. Nearly all Lewis bases (i.e., substances having an unshared pair of electrons) can be ligands in metal complexes. Some typical useful ligands include the halides, e.g., chloride, bromide, fluoride, nitrite, water, amino, etc., including such common ligands as those referred to on page 44 of Basolo et al., supra. The lability of a complex is influenced by the nature of the ligands selected in forming said complex.

Particularly useful cobalt and chromium complexes have a coordination number of six and which have a ligand selected from the group consisting of ethylenediamine (en), diethylenetriamine (dien), triethylenetetraamine (trien), amine (NH₃), nitrate, nitrite, azide, chloride, thiocyanine, isothiocyanate, water, carbonate and ethylenediaminetetraacetic acid (EDTA). The preferred cobalt complexes comprise: (1) at least two ethylenediamine ligands, or (2) at least five amine ligands, or (3) one triethylenetetraamine ligand. Especially useful are the cobalt hexammine salts (e.g. the chloride, bromide, sulfate, sulfite, perchlorate, nitrite and acetate salts). Some specific highly useful cobalt and chromium complexes include those having one of the following formulas:



wherein X represents one or more anions and Y represents one or more cations determined by the charge neutralization rule. Complexes of various other metals, such as complexes of R^{III}, Pt^{IV}, Pd^{IV} and Ir^{III}, which have reactivities similar to the complexes listed above, could be used in the practice of this invention. The redox equilibria published in Stability Constants of Metal-Ion Complexes, Sillen and Martell, published by The Chemical Society, Burlington House, London, England (1964), indicate that the complexes K₂[Pt(Cl)₆], K₂[Pt(OH)₆], K₂[Pd(Cl)₆]

and $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_3$ would have reactivities similar to the cobalt complexes mentioned above.

The metal complex should not be directly and completely reduced by the developing agent prior to or during processing. Some complexes, such as $\text{K}_3[\text{Co}(\text{ox})_3]$ and sodium cobaltinitrite are directly reduced by common developing agents and are not useful therewith. However, there may be a redox reaction between the complex and the developing agent in the presence of metallic silver, which may catalyze, a redox reaction between some complexes and some developing agents. In addition, some complexes, such as certain cobalt hexammine (III) complexes, will undergo a partial redox reaction with certain strong developing agents, but a sufficient amount of unreacted complex will remain to effectively accelerate development. A high degree of stability between the complex and the developing agent is not required when the complex is in contact with the developing agent for a short period, such as when the complex is incorporated in the photographic element or when the complex is added to the developer solution just prior to development.

The metal complexes employed can be incorporated in the light-sensitive photographic silver halide emulsion or, preferably, in the photographic developer solution. When the complex is to be employed in the developer solution, the complex should be so chosen that it remains in the developer solution. The complex should not precipitate out of the developer solution. The amount of metal salt used will vary depending upon the degree of development increase desired, the particular developing agent used and the temperature of development. Generally, good results are obtained when the metal complex is present in the developer solution in concentrations of 10^{-5} up to saturation (generally under 1 molar), and preferably in a molar concentration of about 10^{-4} to 10^{-1} molar.

The photographic developing agents utilized in the practice of this invention include typical black-and-white developers, as 1-phenyl-3-pyrazolidones and aromatic primary amine color developing agents such as p-phenylenediamines. Typical color developing agents include

3-acetamido-4-amino-N,N-diethylaniline,
p-amino-N-ethyl-N- β -hydroxyethylaniline sulfate,
p-aminoethyl- β -hydroxyaniline,
N,N-diethyl-p-phenylenediamine,
2-amino-5-diethylaminotoluene,
N-ethyl- β -methanesulfonamidoethyl-3-methyl-4-aminoaniline,
4-amino-N-ethyl-3-methyl-N-(β -sulfoethyl)aniline,
4-amino-3-methyl-(N-ethyl-N- β -methyl) aniline

and the like. See Bent et al, JACS, Vol. 73, p. 3100-3125 (1951), for further typical, useful color developing agents. The amount of accelerator is generally greatest with the stronger developing agents. Some complexes, such as the cobalt hexammine (III) complexes, function as antifoggants. These antifoggants are preferably used with strong developing agents, especially when large (over about 1.0μ), silver halide grains are being developed, in order to obtain a good increase in the rate of silver development.

The photographic developing solution utilized can contain other conventional addenda such as restrainers, preservatives, antifoggants, stabilizers, silver halide solvent, other accelerators, hardeners and the like.

The processes of this invention are suitable for the development of any of the light-sensitive silver halides, including silver bromide, silver iodide, silver chloride or mixed silver halides such as silver chlorobromide, silver bromoiodide or silver chlorobromoiodide. The invention is useful in accelerating the development of negative, developing out emulsions and reversal silver halide emulsions, such as the silver halide emulsions which contain internal latent images, e.g., those described by Fallesen U.S. Pat. 2,497,875 issued Feb. 21, 1950. The silver halide grains which have internal latent images preferably are

developed in developers which contain a fogging or nucleating agent.

This invention is useful in processing light-sensitive silver halide emulsions which contain various chemical sensitizers, optical sensitizers, stabilizers, speed-increasing compounds, plasticizers, hardeners and coating aids, such as are described and referred to in Beavers U.S. Pat. 3,039,873 issued June 19, 1962, columns 9-12. The light-sensitive silver halide salts can be dispersed in various binders, such as the colloids described and referred to in aforementioned Beavers patent, column 13 and the like. Any suitable support can be used, such as a cellulose ester, poly(ethylene terephthalate), paper, baryta coated paper, polyolefin coated paper such as polyethylene or polypropylene coated paper, which can be treated with a corona discharge to promote emulsion adhesion. Emulsion layers having different speeds can be utilized to extend the latitude of the element.

The following examples are included for a further understanding of the invention.

Examples 1 and 2 illustrate the acceleration of silver development during black-and-white development using a metal complex in accordance with this invention.

EXAMPLE 1

Six samples of a fine grain negative type film comprising a cellulose acetate support having thereon a gelatin-silver bromoiodide emulsion which is 94 mole percent bromide and 6 mole percent iodide, coated at about 360 mg. silver and 1000 mg. gelatin per square foot, are exposed through a 0.3 neutral density step tablet in an intensity scale sensitometer. Samples A, B and C are developed for 2.5 minutes, 5 minutes and 10 minutes, respectively, at 24°C . (75°F .) in a developer composition composition comprising:

	G.
N-methyl-p-aminophenol sulfate -----	6.0
Sodium sulfite -----	50.0
Hydroquinone -----	6.0
Potassium bromide -----	1.0
Water to make 1 liter (pH 9.5).	

The remaining samples D, E and F are developed at 2.5 minutes, 5.0 minutes and 10 minutes, respectively, at 24°C . (75°F .) in the above developing composition containing in addition 5.0 g. of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ per liter.

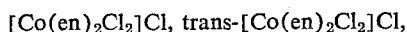
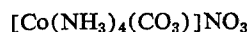
The six processed samples are analyzed for silver by X-ray fluorescent silver analysis techniques. The results, listed in Table 1, show a significantly accelerated rate of silver development afforded by the developer composition containing the cobalt (III) complex according to the present invention. Also, the developer composition of the invention provided improved image-to-fog ratios as compared to the control.

TABLE 1

Sample	Development time, min.	Mg. Ag ^o per square foot
A-----	2.5	120
D-----	2.5	356
B-----	5	179
E-----	5	320
C-----	10	275
F-----	10	356

EXAMPLE 2

Results essentially equivalent to those obtained in Example 1 are obtained when an equivalent amount of $\text{K}_3[\text{Cr}(\text{CN})_6]$, $\text{Na}_3[\text{Co}(\text{CN})_6]$, $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$,



or $[\text{Co}(\text{trien})(\text{NO}_2)_2]\text{NO}_3$ is substituted for the



in the developer composition.

Example 3 illustrates the increased rate of silver developed during black-and-white development of silver halide emulsions containing photographic color coupler, when development is conducted in the presence of a metal complex as described herein.

EXAMPLE 3

Six samples of a single-layer color film having an incorporated color coupler are prepared by coating on a cellulose acetate support, a single layer of a gelatinous silver halide emulsion containing gelatin at 300 mg. per square foot, silver bromiodide at 100 mg. of silver per square foot and 150 mg. per square foot of the color coupler 5- $[\alpha-(2,4\text{-di-tert-amyphenoxy})\text{hexamido}]-2\text{-heptafluorobutyramidophenol}$ dissolved in 75 mg. of dibutyl

Sodium sulfite ----- 40.0
Potassium bromide ----- 0.5
Ethylenediaminetetraacetic acid (EDTA) ----- 8.0
Water to make 1 liter (pH 11.0).

The samples are washed, fixed, washed and dried.
The above procedure is repeated with samples E, F, G and H except that the developer composition contains additionally 2.5 g. of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ /liter in the developer.

Each of the samples contains a composite silver and dye image since the above process does not include a step to bleach the developed silver. The quantity of developed silver in mg. $\text{Ag}^\circ/\text{ft.}^2$ (metallic silver per square foot) and the density of the image dye in the shoulder region and the toe region of the sensitometric curve of each sample is recorded in Table 2 below. The "Dye Yield" is determined by dividing the dye density by the quantity of developed silver.

TABLE 2

Sample	Shoulder (Step 2)			Straight line (Step 9)			Toe (Step 19)		
	Mg. $\text{Ag}^\circ/\text{ft.}^2$	Dye den.	Dye yield	Mg. $\text{Ag}^\circ/\text{ft.}^2$	Dye den.	Dye yield	Mg. $\text{Ag}^\circ/\text{ft.}^2$	Dye den.	Dye yield
A-----	31.6	1.18	.0374	18.6	.77	.0414	2.3	.1	.0435
B-----	48.4	1.68	.0341	26.1	1.06	.0407	2.2	.14	.0637
C-----	59.0	2.08	.0353	35.2	1.45	.0412	7.0	.34	.0486
D-----	68.6	2.32	.0338	46.2	1.9	.0412	20.3	.9	.0443
E-----	33.6	1.34	.0400	19.2	.8	.0416	1.5	.1	.0660
F-----	56.8	2.2	.0388	31.3	1.33	.0425	2.4	.2	.0835
G-----	72.1	3.02	.0419	46.3	2.04	.0440	4.5	.32	.0711
H-----	73.9	3.53	.0485	57.8	2.8	.0485	12.7	.72	.0567

phthalate. The samples are exposed through a 0.3 neutral density step tablet in an intensity sensitometer.

Control samples A, B and C are developed for 2.5 minutes, 5 minutes and 10 minutes at 24°C . (75°F .), respectively, in the developing composition of Example 1. The samples are washed, fixed, washed and dried.

The remaining samples D, E and F are developed at 2.5 minutes, 5.0 minutes and 10 minutes at 24°C . (75°F .), respectively, in the above developer composition containing in addition 5.0 g. of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ per liter. The results show that during the black-and-white developing step, which is the initial step in the processing of a reversal color film, there is a significant increase in the rate of silver development, and an improved image-to-fog ratio due to the presence of the substitution-inert metal complex in the developer solution.

Examples 4 and 5 illustrate the increased dye yield, lower silver fog and accelerated rates of silver development in the color development of silver halide emulsions containing a photographic color coupler, using a metal complex in accordance with this invention.

EXAMPLE 4

Samples A, B, C and D of a coupler-incorporated, single-layer color film such as described in Example 3

The data recorded in Table 2 show that accelerated rates of image silver development, lower silver fog, and high dye yields are obtained in the samples processed with the developing solution containing substitution-inert metal complexes, such as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. When this example is repeated using a photographic element containing separate, overlying silver halide emulsion layers sensitive to blue, green and red radiation, respectively, and containing a yellow dye-forming open-chain ketomethylene photographic coupler, a magenta dye-forming photographic 5-pyrazolone photographic coupler and a cyan dye-forming phenolic photographic color coupler, in the respective blue-, green and red-sensitive layers generally similar increases in increased dye yield, lower silver fog and accelerated rates of silver development are obtained when the cobalt hexammine (III) chloride is present in the developer solution.

EXAMPLE 5

Example 4 is repeated except that the samples are processed at 32°C . (90°F .) Samples J, K, L and M are processed in the developer composition without $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and samples N, O, P and Q are processed in the developer composition with 5.0 g./liter of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ present. The results are presented in Table 3 below:

TABLE 3

Sample	Shoulder (Step 2)			Straight line (Step 9)			Toe (Step 19)		
	Mg. $\text{Ag}^\circ/\text{ft.}^2$	Dye den.	Dye yield	Mg. $\text{Ag}^\circ/\text{ft.}^2$	Dye den.	Dye yield	Mg. $\text{Ag}^\circ/\text{ft.}^2$	Dye den.	Dye yield
J-----	49.1	1.78	.0362	30.3	1.28	.0423	4.9	.26	.0531
K-----	60.4	2.14	.0355	39.4	1.72	.0436	15.5	.7	.0453
L-----	71.6	2.5	.0349	57.4	2.32	.0405	38.4	1.74	.0451
M-----	78.0	2.64	.0338	73.6	2.74	.0430	61.1	2.5	.0409
N-----	61.1	2.22	.0363	37.8	1.68	.0419	3.3	.26	.0788
O-----	73.6	3.12	.0424	54.2	2.44	.0450	9.8	.63	.0643
P-----	76.1	3.7	.0485	67.8	3.24	.0479	24.6	1.38	.0561
Q-----	75.0	3.9	.0520	69.3	3.7	.0535	37.7	2.1	.0561

are exposed through a 0.3 neutral density step tablet in a sensitometer. The samples are processed at 24°C . (75°F .) for 1, 2, 4 and 8 minutes, respectively, in a developer composition comprising:

G.
4-amino-N-ethyl-N- β -hydroxyethylaniline-sulfate -- 20.0
1-phenyl-3-pyrazolidone ----- 0.1

The data in Table 3 show the accelerated rates of silver development, lower silver fog and high dye yields obtained in the practice of this invention.

Example 6 shows that this invention is useful in the development of internal latent image emulsions using fogging developers.

7 EXAMPLE 6

Increases in the rate of silver development, generally similar to the increases obtained in Example 4, are obtained when an internal latent image gelatin silver chlorobromide emulsion, prepared as described in Fallesen U.S. Pat. 2,497,875 issued Feb. 21, 1950, column 2, line 21, to column 3, line 2, is coated on a cellulose acetate support at the rate of 100 mg. silver per square foot, about 300 mg. gelatin per square foot and 100 mg. per square foot of the cyan dye-forming coupler 5- $[\alpha$ -(2,4-di-tert-amylphenoxy) - hexamido] - 2 - heptafluorobutyramidophenol dissolved in 50 mg. of dibutyl phthalate, exposed and developed for 1 minute at 24° C. in the following solution:

Formyl-4-methylphenylhydrazine (nucleating agent) -----	0.1
Na ₂ CO ₃ -----	40.0
Piperidino hexose reductone -----	0.2
5-methylbenzimidazole -----	0.05
4-amino-N-ethyl-N- β -hydroxyethylaniline sulfate --	20.0
[Co(NH ₃) ₆]Cl ₃ -----	1.0
pH -----	12.0
Water to make 1 liter.	

When the above process is repeated, and the quantity of dye is determined, it is noted that the dye density was 2.7. A control prepared in the same way, but without the cobalt hexammine (III) chloride in the developer solution, had a dye density of 0.2. Further, the relative speed of the control was 1.6 as compared to a relative speed of 2.0 when the substitution-inert complex was present in the developer.

This invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. In a photographic process wherein imagewise-exposed, light-sensitive silver halide grains are developed to a metallic silver image with a photographic developing solution containing a photographic developing agent, the improvement wherein said photographic developing solution contains at least a 10⁻⁵ molar concentration of a cobalt- or chromium-ion complex, which complex comprises ligands attached to the central metal ion and at least one cation or anion in ionic association with said complex and which complex, when a test sample thereof is dissolved at .1 molar concentration at 20° C. in an inert solvent solution containing a .1 molar concentration of a tagged ligand of the same species which is uncoordinated, exhibits essentially no exchange of uncoordinated and coordinated ligands for at least 1 minute, said complex having a coordination number of 6, the complex being so chosen that it is not directly reduced by the developing agent.

2. The method of developing a metallic image in an exposed photographic element comprising a cellulose acetate support having coated thereon a gelatin silver bromiodide emulsion which comprises immersing said element in an aqueous photographic developer solution maintained at a temperature of 24° C. and comprising about 5 grams per liter of cobalt hexammine (III) chloride and about 6 grams per liter of methyl-p-aminophenol photographic developing agent.

3. In a photographic process wherein imagewise-exposed, light-sensitive silver halide grains are developed to a metallic image with a photographic developing agent, the improvement which comprises conducting said development in the presence of a metal-ion complex having a coordination number of 6 and having in ionic association therewith at least one anion or cation determined by charge neutralization of said complex, and wherein said metal-ion complex is present in an amount effective

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to increase the rate at which silver forms in the silver development process.

4. A photographic process according to claim 3 wherein said metal-ion complex is a complex which exhibits essentially no change of uncoordinated ligands and coordinated ligands for at least 1 minute when a test sample thereof is dissolved at a 0.1 molar concentration in an inert solvent solution containing a 0.1 molar concentration of a tagged ligand of the same species which is uncoordinated, and said metal-ion complex is a complex which is not directly and completely reduced by the developing agent.

5. A process according to claim 3 wherein said metal ion of said metal-ion complex is capable of existing in at least two valence states.

6. A process according to claim 3 wherein said metal-ion complex is a cobalt complex which comprises (1) at least 2 ethylenediamine ligands, (2) at least 5 amine ligands or (3) at least 1 triethylenetetraamine ligand.

7. A process according to claim 3 wherein said metal-ion complex is a cobalt- or chromium-ion complex.

8. A process according to claim 3 wherein said metal-ion complex is a cobalt hexamine salt.

9. A process according to claim 3 wherein said development is carried out with a solution containing said metal-ion complex in at least a 10⁻⁵ molar concentration.

10. A process according to claim 4 wherein said development is carried out with a solution which contains from about 10⁻⁴ to about 10⁻¹ molar concentration of said metal-ion complex.

11. A process according to claim 3 wherein said photographic developing agent is an aromatic primary amino color-developing agent.

12. A photographic process as defined in claim 3 wherein said silver halide grains have internal latent images and said development is conducted in the presence of a nucleating agent.

13. A photographic process as defined in claim 12 wherein said nucleating agent is formyl-4-methylphenylhydrazine and said complex is cobalt hexammine (III) chloride.

14. A process according to claim 3 wherein said metal-ion complex is an ionic salt of cobalt hexammine (III), hexacyanocobaltate, or [Cr(NH₃)₆]Cl.

15. A process according to claim 3 wherein said photographic developing agent is a black-and-white silver halide developing agent.

16. In a photographic process wherein imagewise-exposed, light-sensitive silver halide grains are developed to a metallic silver image with a photographic developing agent, the improvement which comprises conducting said development in the presence of a cationic or anionic salt of a cobalt- or chromium-ion complex which has a coordination number of 6, wherein said ion complex is present in an amount effective to increase the rate at which silver forms in the silver development process.

17. A process according to claim 16 wherein said metal-ion complex is a cobalt-ion complex which comprises (1) at least 2 ethylenediamine ligands, (2) at least 5 amine ligands or (3) at least 1 triethylenetetraamine ligand.

References Cited

UNITED STATES PATENTS

3,551,406	12/1970	Idelson	96-66 R
3,681,078	8/1972	Pollet et al.	96-66.3
2,497,875	2/1950	Fallesen	96-64

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96-66

Disclaimer

3,748,138.—*Vernon L. Bissonette*, Brockport, N.Y. METAL COMPLEX IN SILVER HALIDE DEVELOPMENT. Patent dated July 24, 1973. Disclaimer filed July 1, 1974, by the assignee, *Eastman Kodak Company*.

Hereby enters this disclaimer to claims 3 through 5, 9 through 12, and 15 of said patent.

[*Official Gazette May 27, 1975.*]