

Dec. 16, 1947.

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2,432,865

PHOTOGRAPHIC ELEMENTS HAVING LIGHT-SENSITIVE SILVER HALIDE
LAYERS CONTAINING IRON, COBALT AND NICKEL DERIVATIVES
OF MERCAPTO TETRAZOLES, TRIAZOLES OR DIAZOLES
Filed June 27, 1945

FIG. 1.

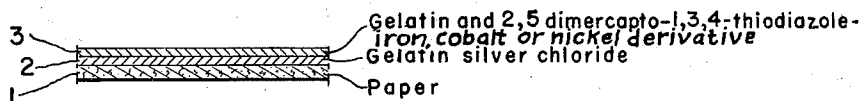


FIG. 2.

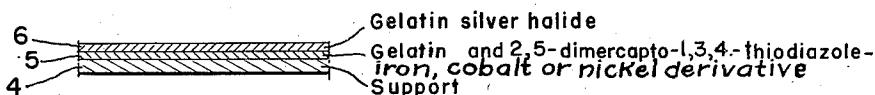


FIG. 3.



FIG. 4.

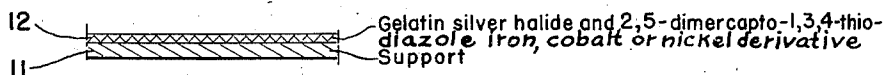
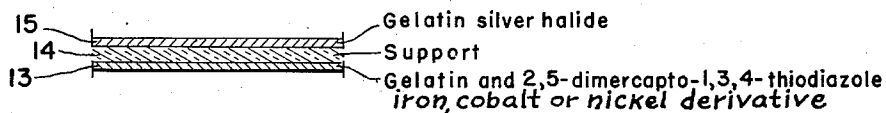


FIG. 5.



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UNITED STATES PATENT OFFICE

2,432,865

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Application June 27, 1945, Serial No. 601,922
In Great Britain January 26, 1945

8 Claims. (Cl. 95—7)

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This invention relates to photographic light-sensitive elements, to compounds which serve as improvers for photographic silver halide emulsions, and particularly to compounds which improve the quality of the developed photographic images obtained in such emulsions.

In the production of photographic images in silver halide emulsions, and particularly in the case of emulsions consisting primarily of silver chloride, the maximum image density obtainable is not always so great as may be desired. Moreover, the common practice of hot-glazing photographic prints tends to affect adversely the image colour, giving a poor quality black which has a "bronzed" appearance, and also reduces the effective maximum density obtainable in the image.

In our United States application Serial Number 573,460 filed January 18, 1945, we have described a method for improving the quality of a photographic image developed in a silver halide emulsion layer in a photographic element, which comprises including in a layer of the element a silver derivative of a compound which in its free state, or in the state of its alkali metal derivative, improves the quality of photographic images developed in such emulsion layers.

It has now been discovered that instead of using a silver derivative of the compound, any other metal derivative of the compound which is soluble or decomposable during treatment of the photographic element with developing and thiosulphate fixing salts may be employed.

According to the present invention, therefore, a process for improving the quality of a photographic image developed in a silver halide emulsion layer in a photographic element comprises adding to such emulsion, or to a colloid medium other than the emulsion which forms a water-permeable layer in such element, a metal (other than silver) derivative of a compound which, when added in its free state, or in the state of its alkali metal derivative, improves the quality of the developed photographic image obtained, the said metal derivative being soluble or decomposable during treatment of the photographic element with developing and thiosulphate fixing baths.

The term "metal derivative" is intended to mean a derivative resulting from replacement

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of hydrogen in the said compound by the metal. Metals which may be employed are, for example, copper, silver, gold, mercury, cadmium, zinc, thallium, aluminium, lead, tin, bismuth, antimony, chromium, uranium, cobalt, iron and nickel. However, not all the metals are equally satisfactory and those which have the least effect on the speed and contrast, and which are therefore preferred are the metals of groups I (b) and VIII of the periodic table of the elements, and in particular copper, gold, iron, cobalt and nickel. Of these, gold and the other rarer elements included in group VIII are generally too expensive for use. Ferric compounds are preferred to ferrous owing to the instability of the latter. The metals of groups II (b) and IV (b), for example zinc, cadmium, mercury, lead and tin, may be used, but generally tend to have some adverse effect on the characteristics of the emulsion, while the metals of group V (b), for example antimony and bismuth, present difficulties in handling. Generally speaking, the best metal to employ appears to be nickel.

In a preferred form of the invention the metal derivatives are added to colloid media which are to be used for coating layers in contact with the silver halide emulsion layer or layers. For example, the metal derivative may be included in a supercoat layer, e. g. a colloid layer coated on top of the photographic emulsion layer and forming, for example, an outer layer of the element, or may be included in a subcoat layer, e. g. a colloid layer lying between a photographic emulsion layer and a support layer, or may be included in an inter-layer between two emulsion layers. It may, however, be present in other layers, for example a backing layer.

It is desirable, especially where the metal derivative is included in a supercoat or in the emulsion layer itself, that it should be in a very fine state of subdivision in the layer in which it is incorporated. Thus, a convenient method of use is to form the metal derivative in situ in the colloid medium in which it is to be dispersed, for example by the double decomposition of a soluble metal salt and an alkali-metal derivative of the compound in a gelatin medium.

The invention may be applied to all varieties of compound which are capable of improving the

quality of the developed image and which will form metal derivatives.

The following are typical classes of compounds which may be used, as their metal derivatives, in accordance with this invention.

(a) Compounds of the type described in British Patent No. 561,875. These are 5-mercapto tetrazoles and specific examples are: 1-phenyl-5-mercapto-tetrazole; 1- α -naphthyl-5-mercapto-tetrazole; 1- β -naphthyl-5-mercapto-tetrazole; 1-p-diethylamino phenyl-5-mercapto-tetrazole; 1-o-methoxy phenyl-5-mercapto-tetrazole; 1-p-chlor phenyl-5-mercapto-tetrazole; 1-benzyl-5-mercapto-tetrazole; 1-cyclo-hexyl-5-mercapto-tetrazole; 1-methyl-5-mercapto-tetrazole; 1-ethyl-5-mercapto-tetrazole.

(b) The 5-mercapto-1.2.4-triazoles described in United States application Serial Number 558,270 filed October 11, 1944.

Specific examples of these are:

1.2-dimethyl-5-mercapto-1.3.4-triazole.
1-ethyl-2-methyl-5-mercapto-1.3.4-triazole
1-phenyl-2-methyl-5-mercapto-1.3.4-triazole
1-phenyl-5-mercapto-1.3.4-triazole
1-benzyl-5-mercapto-1.3.4-triazole
1-methyl-2-ethyl-5-mercapto-1.3.4-triazole
1-methyl-2-n-hexyl-5-mercapto-1.3.4-triazole
1-p-hydroxy phenyl-2-methyl-5-mercapto-1.3.4-triazole.
1-p-amino phenyl-2-methyl-5-mercapto-1.3.4-triazole
1- α -naphthyl-2-phenyl-5-mercapto-1.3.4-triazole
2- α -naphthyl-5-mercapto-1.3.4-triazole
1.2-diphenyl-5-mercapto-1.3.4-triazole

(c) Heterocyclic nitrogen compounds containing two nitrogen atoms in the ring and one, two or three sulphur atoms attached to carbon atoms which are in α -position to the nitrogen atoms (compounds containing a single sulphur atom linked to a carbon atom which is α to both nitrogen atoms are included but are generally less efficient). Examples of this class of compound are:

2.5-dimercapto-1.3.4-thiodiazole
2-mercapto-5-amino-1.3.4-thiodiazole
1-mercapto-4-hydroxy-phthalazine
1.4-dimercapto-phthalazine
2.5-dimercapto-3-methyl-1.3.4-thiodiazole
2-hydroxy-4-mercapto pyrimidine
2:4-dimercapto-pyrimidine
2:4-dimercapto-quinazoline
Trithio barbituric acid

(d) Mercapto hydroxy diazoles, an example of which is:

2-mercapto-4-phenyl-5-hydroxy-1.3.4-thiodiazole

(e) Dimercapto monazoles, an example of which is:

2.4-dimercapto quinoline

(f) Mono mercapto monazoles, examples of which are:

2-mercapto-benzthiazole
2-mercapto-benzoxazole
2-mercapto-quinoline
2-mercapto-6.7-benzbenzthiazole (i. e. naphthathiazole)
4-mercapto-quinoline.

As already indicated, the invention is of particular importance in the case of photo-sensitive elements carrying photographic silver chloride

emulsions, since such emulsions are normally more subject to "bronzing." It may, however, be applied to other silver halide emulsions, e. g. silver chlorobromide, silver bromide and silver iodobromide emulsions. The invention is of particular value in connection with the production of the so-called "contact" printing paper consisting of, or comprising, a silver halide emulsion in which the predominant halide is silver chloride, coated on a paper support.

The following examples illustrate the invention:

EXAMPLE 1

An N/10 solution of 2.5-dimercapto-1.3.4-thiodiazole was prepared in water containing some gelatin. To this was added a quantity of an N/10 solution of a water-soluble salt of the metal to be employed, also containing some gelatin, the quantity being sufficient to give a 5 to 10% excess of the metal ion. These solutions were mixed at 115° F. and the gelatin concentration adjusted so that the final solution contained one part of the metal salt of 2.5-dimercapto-1.3.4-thiodiazole per 5000 parts of the solution, the gelatin strength of the solution being about 2.2%. The solution was coated as a supercoat over a standard gelatin silver chloride emulsion as used in ordinary "contact" or "gaslight" printing paper, the emulsion being carried on a paper support.

This procedure was carried out with a number of different metals and test samples of the dried coatings were exposed behind a density step wedge, developed, and fixed in a thiosulphate fixing bath. Some samples were dried normally and others were dried on a commercial hot-glazing machine. Control samples in which the metal salt of the triazole compound was omitted from the supercoat were similarly processed.

The maximum image density ($D_{\max}$) was determined for each of the various samples and the results obtained are set out in the following Table I.

Table I

Metal	$D_{\max}$ normally dried		$D_{\max}$ hot-glazed	
	Control	Test	Control	Test
Nickel	1.79	1.86	1.56	1.98
Thallium (ous)	1.79	1.87	1.66	2.10
Copper (ic)	1.79	1.87	1.56	2.06
Gold (ic)	1.79	1.87	1.57	1.96
Iron (ous)	1.80	1.86	1.51	1.96
Iron (ic)	1.80	1.84	1.51	1.94
Cobalt	1.80	1.83	1.51	1.95
Aluminium	1.80	1.83	1.51	1.93

All the metal derivatives had a marked effect in reducing the degree of bronzing on hot-glazing and were found to have little deleterious effect on the speed of the emulsion.

In addition to the metals listed in Table I, mercury (ic and ous), tin (ous), cadmium, chromium, lead, uranium, antimony, bismuth and zinc were all found, on similar testing, to give results of the same order as those given in Table I.

The photographic element described in this example is shown in Fig. 1 of the accompanying drawing wherein a paper support 1 carries a gelatino-silver halide emulsion layer 2 which in turn carries a gelatin layer containing an iron, cobalt and nickel derivative of 2, 5-dimercapto-1.3.4-thiodiazole which is designated as layer 3.

The additional photographic elements de-

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scribed above are shown in Figs. 2, 3, 4, and 5 of the accompanying drawing. The element of Fig. 2 consists of a support 4 bearing a layer 5 composed of gelatin which has dispersed therethrough an iron cobalt or nickel derivative of 2,5-dimercapto-1,3,4-thiodiazole on which is deposited gelatino-silver halide emulsion layer 6.

The film element of Fig. 3 consists of a support 7 bearing a gelatino-silver halide emulsion layer 8 on which is coated a layer 9 composed of gelatin having dispersed therethrough an iron, cobalt or nickel derivative of 2,5-dimercapto-1,3,4-thiodiazole. A gelatino-silver halide layer 10 is coated on layer 9.

The element of Fig. 4 consists of a support 11 bearing a gelatino-silver halide emulsion layer 12 which contains an iron, cobalt or nickel derivative of 2,5-dimercapto-1,3,4-thiodiazole. The element of Fig. 5 consists of a support 14 bearing a gelatin layer 13 which contains an iron, cobalt or nickel derivative of 2,5-dimercapto-1,3,4-thiodiazole. The opposite side of the support is coated with a gelatino-silver halide layer 15.

EXAMPLE 2

The procedure indicated in Example 1 was followed using, instead of 2,5-dimercapto-1,3,4-thiodiazole, the compound 2-mercapto-benzthiazole in equivalent amount. The results obtained are set out in the following Table II.

Table II

Metal	D _{max} normally dried		D _{max} hot-glazed	
	Control	Test	Control	Test
Nickel.....	1.75	1.82	1.46	1.97
Thallium (ous).....	1.75	1.88	1.46	1.85
Copper (ic).....	1.75	1.84	1.46	1.70
Gold (ic).....	1.75	1.84	1.46	1.82

In each case the bronzing effect of hot-glazing, very noticeable in the control samples, was substantially entirely absent in the test samples, and the compounds were found to have little deleterious effect on the speed or other characteristics of the emulsion.

It was found that results comparable to those obtained by the procedure of the foregoing examples may also be obtained by the use of any of the other compounds listed under the foregoing headings (a) to (f).

What we claim is:

1. A photographic element comprising a silver halide emulsion layer which has in association with the silver halides thereof, in a water-permeable stratum of the element a metal derivative of a compound selected from the class consisting of 5-mercapto-tetrazoles, 5-mercapto-1,3,4-triazoles, diazoles containing up to three sulphur atoms attached to carbon atoms which are in α -positions to the cyclic nitrogen atoms, mercapto hydroxy diazoles, dimercapto monazoles and mono mercapto monazoles, said metal being taken from the group consisting of iron, cobalt, and nickel.

2. A photographic element comprising a silver halide emulsion layer and, adjacent thereto, a water-permeable colloid layer which contains a metal derivative of a compound selected from the class consisting of 5-mercapto-tetrazoles, 5-mercapto-1,3,4-triazoles, diazoles containing up to three sulphur atoms attached to carbon atoms which are in α -positions to the cyclic nitrogen

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atoms, mercapto hydroxy diazoles, dimercapto monazoles and mono mercapto monazoles, said metal being taken from the group consisting of iron, cobalt, and nickel.

3. A photographic element comprising a silver halide emulsion layer and an outer water-permeable colloid layer adjacent to said emulsion layer, said outer layer containing a metal derivative of a compound selected from the class consisting of 5-mercapto-tetrazoles, 5-mercapto-1,3,4-triazoles, diazoles containing up to three sulphur atoms attached to carbon atoms which are in α -positions to the cyclic nitrogen atoms, mercapto hydroxy diazoles, dimercapto monazoles and mono mercapto monazoles, said metal being taken from the group consisting of iron, cobalt, and nickel.

4. A photographic element comprising a silver halide emulsion layer of which the predominant silver halide is silver chloride which has in association with the silver chloride, in a water-permeable stratum of the element a metal derivative of a compound selected from the class consisting of 5-mercapto-tetrazoles, 5-mercapto-1,3,4-triazoles, diazoles containing up to three sulphur atoms attached to carbon atoms which are in α -positions to the cyclic nitrogen atoms, mercapto hydroxy diazoles, dimercapto monazoles and mono mercapto monazoles, said metal being taken from the group consisting of iron, cobalt, and nickel.

5. A photographic element comprising a silver halide emulsion layer of which the predominant silver halide is silver chloride and, adjacent thereto, a water-permeable colloid layer which contains a metal derivative of a compound selected from the class consisting of 5-mercapto-tetrazoles, 5-mercapto-1,3,4-triazoles, diazoles containing up to three sulphur atoms attached to carbon atoms which are in α -positions to the cyclic nitrogen atoms, mercapto hydroxy diazoles, dimercapto monazoles and mono mercapto monazoles, said metal being taken from the group consisting of iron, cobalt, and nickel.

6. A photographic element comprising a silver halide emulsion layer of which the predominant silver halide is silver chloride and an outer water-permeable colloid layer adjacent to said emulsion layer, said outer layer containing a metal derivative of a compound selected from the class consisting of 5-mercapto-tetrazoles, 5-mercapto-1,3,4-triazoles, diazoles containing up to three sulphur atoms attached to carbon atoms which are in α -positions to the cyclic nitrogen atoms, mercapto hydroxy diazoles, dimercapto monazoles and mono mercapto monazoles, said metal being taken from the group consisting of iron, cobalt, and nickel.

7. A photographic element comprising a paper support carrying a silver halide emulsion layer and an outer water-permeable colloid layer adjacent to said emulsion layer, said outer layer containing a metal derivative of a compound selected from the class consisting of 5-mercapto-tetrazoles, 5-mercapto-1,3,4-triazoles, diazoles containing up to three sulphur atoms attached to carbon atoms which are in α -positions to the cyclic nitrogen atoms, mercapto hydroxy diazoles, dimercapto monazoles and mono mercapto monazoles, said metal being taken from the group consisting of iron, cobalt, and nickel.

8. A photographic element comprising a paper support carrying a silver halide emulsion layer and an outer water-permeable colloid layer adjacent to said emulsion layer, said outer layer

containing a nickel derivative of a compound selected from the class consisting of 5-mercaptotetrazoles, 5-mercapto - 1.3.4 - triazoles, diazoles containing up to three sulphur atoms attached to carbon atoms which are in α -positions to the cyclic nitrogen atoms, mercapto hydroxy diazoles, dimercapto monazoles and mono mercapto monazoles.

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Number
2,066,099
2,221,805
2,377,375

10

Number
390,037

UNITED STATES PATENTS

Number	Name	Date
2,066,099	Dieterle	Dec. 29, 1936
2,221,805	Leermakers	Nov. 19, 1940
2,377,375	Russell	June 5, 1945

FOREIGN PATENTS

Number	Country	Date
390,037	Great Britain	Mar. 30, 1933

REFERENCES CITED

The following references are of record in the file of this patent: