United States Patent

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[54] **METHOD FOR FIXING LIGHT-SENSITIVE FREE RADICAL PHOTOGRAPHIC MATERIALS WITH HEAVY METAL SALTS**

4 Claims, No Drawings

[52] **U.S. Cl.** **96/48,** 96/90

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[50] **Field of Search** 96/88, 89, 90, 48

[56] **References Cited**

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ABSTRACT: Images formed in free radical photosensitive materials comprising organic halogen-containing photoactivators capable of generating halogen free radicals upon exposure to light are fixed by treatment with aqueous solutions of reducing heavy metal salts.

METHOD FOR FIXING LIGHT-SENSITIVE FREE RADICAL PHOTOGRAPHIC MATERIALS WITH HEAVY METAL SALTS

This invention relates to a method for fixing light sensitive photographic materials, characterized in that a light sensitive photographic material containing an halogen-containing photoactivator capable of forming a halogen free radical by action of light and, in admixture therewith, a chromotropic agent showing a visible color change by action of said free radical is subjected to image wise exposure to form an image and is then treated with a reducing heavy metal salt. An object of the present invention is to provide a fixing method which has no detrimental effect on the resulting image, is simple in operation and gives no harm to the human body.

As methods for fixing this kind of light sensitive photographic material, there have heretofore been known a heat fixing method and a solvent fixing method. The heat fixing method is carried out in such a manner that the light sensitive photographic material is subjected to image wise exposure to form an image and is then heated to decompose or sublimate the composition which has been left without taking part in the image formation, so that no color change is caused any more even when the image is exposed to light.

As light sensitive photographic materials which are effectively treated according to said heat-fixing method, there are those containing a light sensitive composition composed mainly of diphenylamine and carbon tetrabromide or "Brilliant green" and carbon tetrabromide. Further, as the photoactivator agents, aroyl trihalogenated hydrocarbons have been recommended in addition to carbon tetrabromide. As is well known, however, carbon tetrabromide is extremely toxic and its permissible amount per day is about 1 p.p.m. Therefore, a special consideration is necessary so as not to inhale its vapor during the heat treatment. Thus, carbon tetrabromide is not desirable for practical use. Further, aroyl trihalogenated hydrocarbons are strongly lachrymatory and are vaporized on heating, and therefore they are not desirable as in the case of carbon tetrabromide. According to the heat fixing method, light sensitive photographic materials are heated to decompose or sublimate the compositions, as mentioned above. Therefore, light sensitive materials to be treated with this method should contain components which are readily decomposable and sublimatable. It is, however, well known that ordinarily, components having such properties are more or less decomposed or sublimated even at normal temperature. The heat-fixing method, therefore, is applicable only to light sensitive photographic materials low in storability and is not suitable for those high in storability.

On the other hand, the solvent fixing method is carried out in such a manner that a composition, which has been left without taking part in the formation of image, extracted with a suitable solvent, so that no color change occurs even when the image is reexposed. In this method, therefore, it is necessary to use a solvent which readily dissolves only the composition left without taking part in the image formation but does not dissolve the formed image at all. If there is used a solvent which dissolves the image even to a slight extent, the image runs by treatment therewith, whereby the reproduction is lowered in resolving power. Therefore, solvents which satisfy the above object are greatly restricted and the selection of suitable solvent is extremely difficult. Moreover, the solvent fixing method is a process in which a so-called nonimage portion is washed. Accordingly, in order to effect the washing completely, the washing solvent should be used in a large amount or should be frequently exchanged and a large cost is required therefore. Thus, the solvent fixing method is not practical, either.

The present invention is a fixing method, which has overcome all the above drawbacks. In the present method, a reducing heavy metal salt is used as a fixing agent, and a light sensitive photographic material, which has been exposed, is either coated with or is immersed in an aqueous solution of said salt. The fixing agent employed in the present invention neutralizes by chemical action the activity of any photoactivator which has not taken part in the formation of image, and is considered to capture halogens present in the components of the optically active agent to make said agent inert to light.

Typical compounds as such fixing agents are stannous chloride, stannous bromide, stannous iodide, titanic chloride, ferrous sulfate, titanic sulfate, vanadous sulfate, chromous chloride and chromous sulfate.

According to the present invention, the above-mentioned fixing agent is formed into an aqueous solution at a concentration of about 5–40 percent, and a light sensitive photographic material, which has been exposed, is either coated with or is immersed in said aqueous solution. In the case of coating, the amount of fixing solution to be applied is affected by the kind of optically active agent and the thickness of light sensitive layer, but the fixing solution may be applied in such an amount as used in the color development of wet type diazo copying paper, i.e. in such an amount as to wet the surface of the photographic paper, and, in practice, it may be said that the amount is as employed in a semidry diazo process. In this case, the fixing solution may be incorporated with a binder such as a cellulose derivative, vinyl polymer or synthetic rubber. In the case of immersion, the treatment may be effected in the same manner as in the developing and fixing treatments of silver halide light sensitive materials. The concentration of fixing solution and the treating time are affected by the kind of photoactivator and the thickness of light-sensitive layer and are not definite. Ordinarily, however, favorable results are obtained when the treatment is effected for several seconds to several minutes.

In applying the fixing solution onto the surface of a light sensitive photographic material, the adoption of a somewhat higher concentration than in the case of immersion results in more favorable fixing effects. However, if a light sensitive photographic material, which has been coated with or immersed in the fixing solution, is heated and dried at a temperature of 100°–180°C. (by means of a hot roll or hot plate having a surface temperature of 100°–180°C.), the fixing effects are further enhanced and the concentration of the fixing solutions can be lowered.

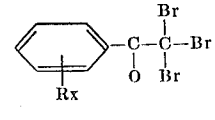
If the fixing solution is incorporated with about 2–20 percent of a compound capable of increasing the reducing ability of the reducing heavy metal salt employed, such as hydrochloric acid, caustic soda or acetic acid, the amount of the fixing agent can advantageously be reduced. Further, if the fixing solution has been incorporated with 2–15 percent of a complex compound-forming agent such as potassium chloride or potassium iodide, or a buffer agent such as sodium carbonate or borax, the storability (life) of the fixing solution can be prolonged ordinarily to several times the life of a fixing solution not incorporated with such compound. According to the present method, the fixing solution is further incorporated with about 2–10 percent of a reducing agent such as hydroquinone or metol to prevent the background of image from discoloration due to compounds formed by the fixing.

As mentioned above, the fixing solution employed in the present invention may be incorporated with 2 or 3 assistant components.

Examples of useful photoactivators are as follows:

i. Compounds represented by the general formula $R—CX_3$ wherein R is an aryl, arkyl, aralkyl, aroyl or alkenyl group or a hydrogen or halogen atom; and X is a halogen atom, such as for example, carbon tetrachloride, carbon tetrabromide, hexachloroethane, pentabromoethane, p-nitrobenzotribromide, bromotrichloromethane, hexabromoethane, benzotrichloride, iodoform, tetrachlorotetrahydronaphthalene, chloral, bromal, 1,1,1-tribromo-2-methyl-2-propanol, 1,1,2,2-tetrabromoethane, 2,2,2-tribromoethanol, trichloroacetamide, 1,1,1-trichloro-dimethyl-2-propanol and α,α,α-trichlorotoluene.

ii. Compounds represented by the general formula



wherein R is a hydrogen atom or 1–5 substituents on the benzene ring, said substituents being any of nitro, halogen, alkyl, haloalkyl, acetyl, haloacetyl, alkaryl and alkoxy groups, and not all of the substituents are required to be same, such as for example, O-nitro-α,α,α,-tribromoacetophenone, m-nitro-α,α,αα,α,α-tribromoacetophenone,α,,α-m-tetrobromoacetophenone,α,α,α-tribromo-3,4-dichloroacetophenone ,α,α,α-p-tetromoacetophenone, and α,α,α,α,α,α-hexabromo-p-diacetylbenzene.

iii. Compounds represented by the general formula

$$R—SO_2—X$$

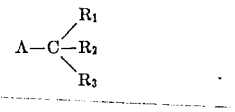
wherein R is an alkyl group or aryl group (including the case where the group has a substituent); and X is a halogen atom, such as for example, 1,3-benzenesulfonyl chloride, 2,4-dinitrobenzenesulfonyl chloride, o-nitrobenzenesulfonyl chloride, m-nitrobenzenesulfonyl chloride, 3,3-diphenylsulfonedisulfonyl chloride, ethanesulfonyl chloride, p-bromobenzenesulfonyl chloride, p-nitrobenzenesulfonyl chloride, p-iodobenzenesulfonyl chloride, p-acetamidebenzenesulfonyl chloride, p-toluenesulfonyl chloride, methanesulfonyl chloride, benzenesulfonyl chloride, m-nitrobenzenesulfonyl fluoride and benzenesulfonyl bromide.

iv. Compounds represented by the general formula

$$R—S—X$$

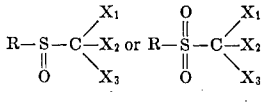
wherein R is an alkyl group or aryl group (including the case where the group has a substituent and X is a halogen atom); and X is a halogen atom, such as for example, 2,4-dinitrobenzenesulfinyl chloride and o-nitrobenzenesulfenyl chloride.

V. Compounds represented by the general formula



wherein A is a heterocyclic compound residue which may have a substituent; R_1, R_2 and R_3 are individually a hydrogen, chlorine or bromine, and not all of them are hydrogen atoms at the same time, such as for example, w,w,w,-trioromoquinaldine, w,w-dibromoquinaldine, 2-w,w,w,-tribromomethyl-4-methylquinoline, w,w,-dichloromethylquinoline, w-bromolepidine, 2-w-bromomethyl-isoquinoline, 4-w,w,w-tribromomethylpyrimidine, 4-phenyl-6-w,w,w,-tribromomethyl-pyrimidine, 2-w,w,w,-trichloromethyl-6-nitrobenzothiazole, 1-phenyl-3-w,w,w-trichloromethyl-pyrazole, w,w,w-tribromolepidine-chromomethylate, α-w,w-dibromomethyl-4-chloropyridine, 1-methyl-2-chloromethyl-benzimidazole and 2.5-ditribromomethyl-3.4-dibromothiophene.

vi. Compounds represented by the general formula



wherein R is a substituted or unsubstituted aryl group or heterocyclic residue; X_1, X_2 and X_3 are individually a hydrogen, chlorine or bromine atom, and not all of them are hydrogen atoms at the same time, such as for example, hexabromodimethyl sulfoxide, pentabromodimethyl sulfoxide, hexabromodimethyl sulfone, trichloromethyl-phenylsulfone, tribromomethyl-phenylsulfone, trichloromethyl-p-chlorophenylsulfone, tribromomethyl-p-nitrophenylsulfone, 2-trichloromethylbenzothiazolylsulfone-(2), 4.6-dimethyl-pyrimidyl-2-trioromomethylsulfone, tetrobromodimethylsulfone, 2.4-dichlorophenyl-trichloromethylsulfone, 2-methyl-4-chlorophenyl-trichloromethylsulfone, 2.5-dimethyl-4-chlorophenyl-trichloromethylsulfone and 2.4-dichlorophenyl-tribromomethylsulfone.

There are generally two kinds of chromotropic agents. One is a color-forming agent employed as the so-called negative-positive-type which originally is a colorless substance but is convertible into a colored state by action of a free radical formed from the above-mentioned optically active agent. The other is discoloring agent employed as the so-called positive-positive-type which originally is colored but, by action of said free radical, the color is changed to another color or is decolored to colorless. Examples of such chromotropic agents are amine compounds such as diphenylamine, dibenzylamine, triphenylamine, N-hydroxyethyl-N-ethylaniline and P.P'-methylenebis (N,N-diethylaniline); leuco-base dyes such as Leucomalachite green, Michler's hydrol and Leucomethylene Blue; and dyes of the diphenylmethane, triphenylmethane, thiazine, oxazine, xanthene, anthraquinone, iminonaphthoquinone and azomethine types.

Further, there may be included in the photosensitive compositions additives such as sensitizers, color tone-improving agents and vehicles, and even in the case of light sensitive photographic materials incorporated with such additives, the present method effectively displays the fixing effects.

In short, in accordance with the present method, a light sensitive photographic material which has been exposed may merely be coated with or immersed in an aqueous solution of such fixing agent as mentioned above and, if necessary, may be heated and dried after fixing. The present method, therefore, is free from such drawbacks as generating a poisonous gas or dissolving an image formed to lower the resolving power of the image, as seen in the conventional method, i.e. the method in which the fixing is effected by mere heating or the solvent fixing method in which an expensive solvent is used in a large amount. Accordingly, the operation is effected in a simple manner and excellent stable copies can be formed.

The following examples illustrate the present invention.

EXAMPLE 1

A photographic baryta paper was coated under a red safety lamp with a sensitive liquid having the composition as shown below and was then dried.

Hexabromodimethylsulfone	2.5 g.
Diphenylamine	5.0 g.
Acetone	100 cc.

On the thus obtained light sensitive photographic material was placed a photographic negative original sheet, and the material was exposed to a 800 w. mercury lamp for 5 seconds at a distance of 5 cm., whereby a deep blue positive image with a white background was obtained.

Subsequently, the photographic material bearing said image was immersed for one minute in a fixing solution of the composition shown below to obtain a copy entirely stable to light.

Composition of fixing solution:	
Stannous chloride	5 g.
Hydrochloric acid	1 cc.
Water	100 cc.

Further, when the image-bearing photographic material was treated with a fixing solution prepared by incorporating 3 g. of hydroquinone to the above fixing solution, no discoloration in background was seen even when the image had been stored for a long period of time.

Example 2

In the same manner as in example 1, a sensitive liquid having the composition shown below was applied onto a photographic baryta paper.

w,w,w,-Tribromoquinaldine	2.5 g.
N-Hydroxyethyl-N-ethylaniline	5.0 g.
Acetone	100 cc.

The thus obtained light sensitive photographic material was exposed in the same manner as in example 1, and was then coated, using a wet-type diazo developing means, with a fixing solution having the composition shown below to such an extent that the surface of the photographic material was wetted, whereby a blue image entirely stable to reexposure was obtained.

Stannous bromide	10 g.
Hydrochloric acid	2 cc.
Water	100 cc.

Further, when the photographic material in a wet state by application of the fixing solution was heated and dried at 150° C. for 7 seconds, the resulting image was stable as in the above case. In this case, however, sufficiently effective fixing could be attained even when there was used a fixing solution having a composition lowered in concentration of the fixing agent as shown below.

Stannous bromide	7 g.
Hydrochloric acid	2 cc.
Water	100 cc.

Example 3

In the same manner as in example 1, a sensitive liquid having a composition as shown below was applied onto a photographic baryta paper.

Carbon tetrabromide	5 g.
Diphenylamine	5 g.
Cellulose acetate	2 g.
Acetone	100 cc.

The thus obtained light sensitive photographic material was exposed in the same manner as in example 1 to immediately obtain a blue image.

Subsequently, the photographic material bearing said image was immersed for 1 minute in a fixing solution having the composition shown below, whereby the image became stable to reexposure.

Stannous chloride	10 g.
Tartaric acid	5 g.
Aerosol MA	0.1 cc.
Water	100 cc.

(aerosol MA is an anion surface active agent produced by American Cyanamid Co.)

Further, when the above fixing solution was incorporated with 5 g. of a metallic zinc powder, the life of the fixing solution was prolonged to about 5 times.

Example 4

A white base, which had been surface-treated with a 10 percent aqueous solution of a polyvinyl alcohol having a polymerization degree of 600, was coated with a sensitive liquid having the composition shown below to prepare a bluish green colored light-sensitive photographic material.

Tribromomethylphenylsulfone	5 g.
Ethylaminophenylimino-naphthoquinone	2.5 g.
Cellulose acetate	1 g.
Acetone	100 cc.

This photographic material, which was of the positive-positive type, was exposed in the same manner as in Example 1, whereby the exposed portion was decolored and a clear bluish green image was obtained. The photographic material was coated, using a quick copying development and stabilization means, with a fixing solution having the composition shown below to such an extent that the surface of the photographic material was wetted, whereby an image entirely stable to reexposure was obtained.

Stannous chloride	10 g.
Tepol 610	0.1 g.
Water	100 cc.

(Tepol 610 is an anion surface active agent produced by Shell Oil Co.).

Example 5

In the same manner as in example 1, a sensitive liquid having the composition as shown below was applied onto a photographic baryta paper.

2.5-Dimethyl-4-chlorophenyl-trichloromethylsulfone	5 g.
Diphenylamine	10 g.
Acridine Orange	0.1 g.
Acetone	100 cc.

The light sensitive photographic material thus obtained contains a sensitizing coloring matter and hence is sensitive even to a visible ray zone. Therefore, the photographic material was exposed for 15–20 seconds at a distance of 30 cm., using a photographic negative as an original sheet, by means of a slide projector having a 300 w. tungsten bulb as a light source, whereby a blue positive image was obtained. Using the same means as in example 2, the photographic material bearing said image was subjected to fixing treatment with a fixing solution having the composition shown below to obtain a copy having an image entirely stable to reexposure.

Stannous chloride	5 g.
Caustic soda	1.5 g.
Water	100 cc.

Example 6

The same light-sensitive photographic material as in example 1 was exposed in the same manner as in example 1 and was immersed for 1 minute in a fixing solution having the composition shown below to obtain a copy entirely stable to reexposure.

Ferrous sulfate	10 g.
Water	100 cc.

What is claimed is:

1. In a process for forming a permanent image which comprises exposing imagewise to a light copy sheet comprising a composition comprising an organic halogen-containing photoactivator compound responsive to light exposure to produce halogen free radicals and a chromotropic agent capable of producing a visible color change by the action of said free radicals, thereby forming in said composition a visible color-change image corresponding to said light-exposure, and treating said material to render said composition incapable of further color change upon exposure to light, thereby fixing said color-change image; the improvement which comprises treating said composition after said image-wise light-exposure with an aqueous solution of a reducing salt of a heavy metal selected from the group consisting of tin, titanium, iron, vanadium, and chromium for a time sufficient to render said photoactivator incapable of producing said halogen free radicals upon light-exposure, thereby fixing said color-change image.

2. The improvement according to claim 1 wherein said aqueous solution comprises between about 5 and 40 percent of a heavy metal salt selected from the group consisting of stannous chloride, stannous bromide, stannous iodide, titanic chloride, ferrous sulfate, titanic sulfate, vanadous sulfate, chromous chloride and chromous sulfate.

3. The improvement according to claim 2 wherein said aqueous solution additionally comprises between about 2 and 10 percent of an organic reducing agent selected from the group consisting of metol and hydroquinone.

4. The improvement according to claim 1 wherein said treating step comprises wetting said composition with said aqueous solution and drying the resulting wetted composition at a temperature between about 100°–180° C.

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