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[54] **SILVER COMPLEX DIFFUSION TRANSFER
PROCESS UTILIZING AN AROMATIC
DISULFIDE**

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[58] **Field of Search** 96/29, 109

[56] **References Cited**

UNITED STATES PATENTS

3,043,696 7/1962 Herz et al. 96/109

3,062,654	11/1962	Allen et al.	96/109
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[57]

ABSTRACT

A method of stabilizing the image-tone of silver images formed according to the silver complex diffusion transfer process is described, which comprises either carrying out the diffusion transfer process in the presence of an aliphatic, aromatic or heterocyclic disulphide having at least one water-solubilizing group in acid or salt form or treating the image-receiving element subsequent to the formation therein of the silver complex diffusion transfer image with a solution of the said disulphide.

8 Claims, No Drawings

SILVER COMPLEX DIFFUSION TRANSFER PROCESS UTILIZING AN AROMATIC DISULFIDE

The present invention relates to the formation of silver images by the silver complex diffusion transfer process.

The principle of the silver complex diffusion transfer process is described in British Pat. No. 614,155 filed Nov. 2, 1939 by Gevaert Photo-Producten N.V., its first Patent of Addition 654,630 filed Sept 4, 1946 by Gevaert Photo-Producten N.V. and in German Pat. No. 887,733 filed Jan. 24, 1941 by Agfa A.G. This process comprises the steps of exposing a photosensitive element containing a silver halide emulsion layer, developing the exposed photosensitive silver halide emulsion layer and forming a soluble silver complex of unexposed silver halide by treating the said photosensitive silver halide emulsion layer with an alkaline processing fluid in the presence of a developing agent and a silver halide complexing agent, transferring said soluble silver complex by diffusion to the silver receptive layer of an image-receiving element in superposed relationship with said silver halide emulsion, forming at said silver receptive layer an image incorporating silver from said silver complex under the action of development nuclei, and separating said image-receiving element from said photosensitive element.

According to a typical embodiment of the silver complex diffusion transfer process suitable for in-camera processing a composite material of unitary structure is used which comprises a photosensitive element, an image-receiving element and a viscous processing fluid contained in a pod or container. After image-wise exposure of the photosensitive element, which comprises a silver halide emulsion layer, the superposed elements e.g. the photosensitive element and the image-receiving element are guided between a pair of pressure rollers whereby the viscous processing liquid is spread as a uniform layer between the photosensitive element and the image-receiving element. The photosensitive element and the image-receiving element are maintained in superposed relation for a determined period, usually of the order of 10 to 20 seconds, during which the exposed silver halide is developed, the undeveloped silver halide is converted into a water-soluble complex silver salt and the said complex is transferred through the layer of processing liquid to the silver precipitating layer of the image-receiving element where it is converted into a visible print. At the end of this contact period the photosensitive element is separated by stripping from the image-receiving element. Elements suitable for use in this silver complex diffusion transfer process are described in detail e.g., in U.S. Pat. Specification No. 2,543,181 of Edwin H. Land, issued Feb. 27, 1951.

The silver complex diffusion transfer process is generally carried out in the presence of compounds which influence the tone of the silver deposited in the image-receiving layer so that images are obtained possessing a black or bluish-black tone instead of yellow to brown tone.

Even though black or bluish-black diffusion transfer images are formed, the tone of the images is subject to alteration upon storing probably owing to aerial oxidation, which results in a change of image tone from black of bluish-black to yellow or brown; these changes

in image-tone are particularly dependent on the conditions under which the images are stored.

It has now been found that the tone of images formed according to the diffusion transfer process can be stabilized against alteration by carrying out said process in the presence of aliphatic, aromatic or heterocyclic disulphides comprising at least one water-solubilizing group such as a carboxyl group and a sulpho group in acid or salt form, or by treating the image-receiving element subsequent to the formation of the image with a solution of one or more of said disulphides.

Particularly suitable disulphides for use according to the present invention can be represented by the following general formula :



wherein :

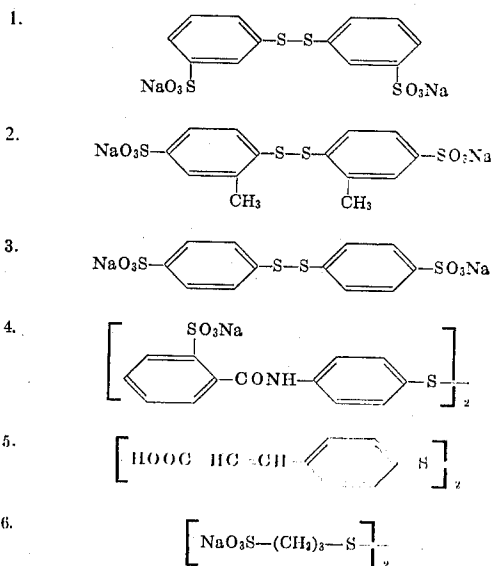
A_1 and A_2 each represents alkylene, preferably C_1 - C_7 alkylene which may or may not be substituted e.g. by alkyl and aryl, or preferably arylene e.g., phenylene which may or may not be substituted e.g., by alkyl, alkoxy, halogen or a water-solubilizing group for example sulpho and carboxyl in acid or salt form, and

X and Y each represents a water-solubilizing group for example sulpho and carboxyl in acid or salt form or a substituent carrying such water-solubilizing group the said substituent being for example a saturated or unsaturated hydrocarbon group such as vinyl, a heterocyclic group such as benzimidazolyl, the group $-CONHR_1$ or $-SO_2NHR_1$ wherein R_1 stands for alkyl or aryl or the group

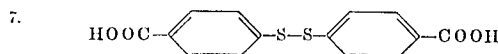
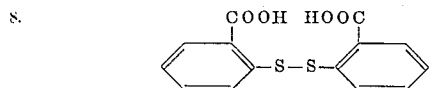
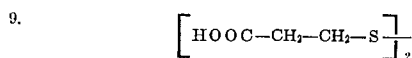
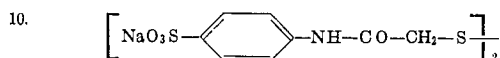
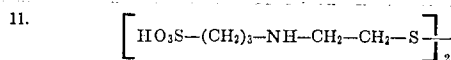
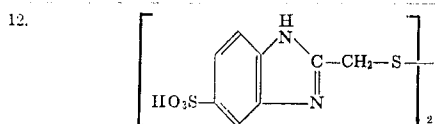


wherein R_2 stands for hydrogen or C_1 - C_5 alkyl and R_3 stands for C_1 - C_5 alkyl or an acyl group of a carboxylic or sulphonic acid such as benzoyl, benzenesulphonyl, propionyl, etc.

Typical disulphides of use according to the present invention are :



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Compounds 1, 2 and 3 can be prepared according to the method described by H.A. Smith, G.Doughthy and G.Gorin in J. Org. Chem. 29 (1964) 1484.

Compound 4 was prepared as follows :

7.44 g (0.03 mole) of 4,4'-dithioaniline and 16.5 g (0.09 mole) of o-sulphobenzoic anhydride were boiled for 11 hours in 150 ml of pyridine. The solution was concentrated by evaporation whereupon the residue was dissolved in water and neutralized with sodium carbonate. The solution was again concentrated by evaporation and the pyridine residues were removed. The residue was recrystallized from 100 ml of water. Yield : 8 g (40 percent). Melting point : >260°C.

Compound 5 can be prepared as described in J.Org.-Chem. 27 (1962) 2840.

Compound 6 can be prepared as described in US Pat. No. 3,057,725 of Arthur H.Herz and Norman W.Kalenda issued Oct. 10, 1962.

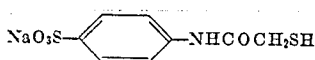
Compound 7 can be prepared as described in J.Soc.-Chem. Ind. 44 (1925) 196.

Compound 8 can be prepared as described in Org.-Syn.Coll. Vol. II, 580 (1943).

Compound 9 can be prepared as described in J.Am.-Chem. Soc. 57 (1935) 45.

Compound 10 was prepared as follows :

26.9 g (0.1 mole) of the compound with formula



(cf. Analytical Chemistry 31, 918 (1959) and 4 g (0.1 mole) of sodium hydroxide were dissolved in 250

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ml of water. At room temperature, a solution of 15 g (0.1 mole) of sodium iodide and 12.7 g (0.05 mole) of iodine in 100 ml of water was added dropwise. After having left standing overnight, the residue was washed with methanol in order to dissolve sodium iodide. The product was recrystallized from water/methanol. Yield : 18 g (66 percent). Melting point : >260°C.

Compound 11 was prepared as follows :

To a solution of 38 g (0.25 mole) of cystamin (free base) in 250 ml of anhydrous methanol, a solution of 61 g (0.5 mole) of propane sultone in 250 ml of anhydrous methanol was added where-upon the whole was boiled for 3 hours. The hygroscopic oil which precipitated was purified by means of the ion exchanger Amberlite IR/20. Yield : 48 g (50 percent). Melting point : 200°C.

Compound 12 was prepared as follows :

48.8 g (0.2 mole) of 2-mercaptomethylbenzimidazole-5-sulphonic acid and 21.2 g (0.2 mole) of sodium carbonate were dissolved in 400 ml of water. A solution of 33.2 g (0.2 mole) of potassium iodide and 25.4 g (0.1 mole) of iodine in 200 ml of water was added dropwise at room temperature whereupon the solution was acidified with an excess of hydrochloric acid. The precipitate formed was purified by dissolution in diluted ammonium hydroxide and reprecipitation by means of hydrochloric acid. Yield : 30 g (60 percent). Melting point : >260°C.

One of the advantages of the compounds of the invention over other compounds suitable for stabilizing the image-tone of diffusion transfer images is that their effectiveness is independent of the location of the compound so that even though they are used to stabilize the transfer image in the image-receiving element they can be incorporated in the light-sensitive element where most of the other image-tone stabilizing compounds are ineffective. Moreover, as is known in the art while being present in the light-sensitive silver halide element the disulphide compounds also have a stabilizing and antifogging effect with respect to the silver halide emulsion of the light-sensitive element. Thus, the disulphide compounds used according to the present invention in order to stabilize the image-tone of images produced according to the silver complex diffusion transfer process may be present during the diffusion transfer image formation in the processing solution and/or the image-receiving element and/or the light-sensitive element. However, favourable results are also obtained when the image-receiving element is treated subsequently to the formation of the image with a solution of one or more of said compounds in a suitable solvent e.g., water or an alcohol such as ethanol and methanol.

The amount of compound to be used in accordance with the present invention depends on the particular compound involved and the location of the compound in carrying out the diffusion transfer process. This amount can vary between very wide limits and the optimum amount is best determined for each particular case by trial. When located in the photosensitive silver halide element, the most suitable concentration is generally comprised between about 5 mg and about 200 mg, preferably between 10 mg and 70 mg per sq.m. When used in the image-receiving element, the pro-

cessing solution or another solution for treating the final image, generally lower amounts suffice.

The silver halide emulsions utilised in preparing photosensitive elements used in the present diffusion transfer system can be any of the conventional negative-type emulsions. Typical suitable silver halides include silver chloride, silver bromide, silver bromoiodide, silver chloroiodide, silver chlorobromide, silver chlorobromoiodide, etc. These silver halide emulsions can contain spectral sensitizers, speed-increasing addenda, hardeners, coating aids, antifoggants, plasticizers and the like conventional emulsion addenda.

As previously noted, processing occurs in the presence of a silver halide complexing agent and a developing agent.

Silver halide complexing agents suitable for use in diffusion transfer processes are well known in the art and include alkali metal thiosulphates and thiocyanates, such as sodium thiosulphate and sodium thiocyanate, as well as cyclic imides for example barbituric acid, uracil and urazole as well as derivatives thereof, examples of which can be found in U.S. Pat. No. 2,857,276 of Edwin H. Land and Helen J. Tracy issued Oct. 21, 1958. These complexing agents can be incorporated into the image-receiving element as well as into the processing fluid. Suitable developing substances are among others: hydroquinone, monomethyl-p-aminophenol sulphate, aminophenol, 3-pyrazolidinone developing substances as well as hydroxylamine derivatives as described in U.S. Pat. Nos. 2,857,276 of Edwin H. Land and Helen J. Tracy issued Oct. 21, 1958, 3,287,124 and 3,287,125 both of Milton Green, Adnan A. Sayigh and Henri Ulbrich both issued Nov. 22, 1966, and 3,293,034 of Milton Green, Adnan A. Sayigh and Henri Ulbrich issued Dec. 20, 1966 for example N,N-diethyl- and N,N-di(2-ethoxy-ethyl)-hydroxylamine. These developing substances can be wholly or partly present in the image-receiving element and/or the photosensitive element. Thus, hydroquinone together with a bisulphite can be present in the image-receiving material, such as described in British Pat. Ser. No. 1,000,115 filed Aug. 4, 1961 by Gevaert Photo-Producten N.V. Also combinations of two or more developing agents can be used successfully, such as the combination of hydroquinone and a 3-pyrazolidinone derivative together in the image-receiving material as described in British Pat. 1,012,476 filed Dec. 18, 1961 by Gevaert Photo-Producten N.V. and the combination of hydroquinone in the image-receiving material and a 3-pyrazolidinone derivative in the light-sensitive material as described in the Belgian Pat. 663,674 filed June 17, 1963 and 635,813 filed Aug. 5, 1963 both by Gevaert Photo-Producten N.V.

The processing fluid comprises bases imparting to the fluid the required alkalinity. As examples of such bases mention may be made of alkali-metal hydroxides, e.g., sodium and potassium hydroxide, sodium carbonate, borax, sodium metaborate, trisodium phosphate, etc.

The fluid may further contain, or dissolve in its travel to the photosensitive element, other compounds which are desired in the treatment of the photosensitive layer and in the production of the positive image in the image-receiving layer.

When the developing and/or silver complexing agents are incorporated in the photosensitive and/or image-receiving element, the development of the exposed silver halide and the formation of the silver com-

plex of unexposed silver halide is activated when an alkaline processing fluid is spread as a thin layer between the photosensitive element and the image-receiving element. As described in British Pat. No. 1,013,343 filed Dec. 29, 1961 by Gevaert Photo-Producten N.V. it is even possible to carry out the silver complex diffusion transfer process by using common water as processing fluid. For this purpose all the ingredients such as developing agents, complexing agents for silver halide, alkali, development nuclei and the like which are necessary in a silver complex diffusion transfer process are incorporated into the photosensitive element and/or the image-receiving element.

In silver complex diffusion transfer processes for in-camera processing, the processing fluid employed is relatively viscous, of the order of 1,000 to 200,000 centipoises at 20°C, so as to be easily controlled when spread. In order to obtain the desired viscosity, the liquid contains a thickening agent, preferably a water-soluble film-forming material such as water-soluble plastic so that when the liquid is removed from the processing layer by absorption and/or evaporation there remains a solid plastic film. The film-forming plastic may be any of the high molecular weight polymers which are stable to alkali and which are soluble in aqueous alkaline solutions, e.g., hydroxyethylcellulose, starch or gum, polyvinylalcohol, the sodium salts of polymethacrylic acid and polyacrylic acid, sodium alginate, sodium carboxymethyl cellulose. As is known in the art, stripping of the silver halide element from the image-receiving element may separate the solidified layer of processing composition from the image-receiving element or may permit the layer of processing composition to remain in contact with the image-receiving element so that the solidified layer provides a protective coating over the image obtained.

The viscous processing fluid for use in in-camera processing is preferably confined within a hermetically sealed container or pod which is positioned between the photosensitive element and the image-receiving element and which is ruptured and releases its contents upon advancing the photosensitive element and image-receptive element between a pair of pressure-rollers. Such a container is impervious to the processing liquid and to the vapour of said liquid, and may be formed of a multilayer composite material comprising as inner layer in contact with the liquid, a material which is impervious to the liquid as intermediate layer a substance which is impervious to the vapour of said liquid and as outer layer a material merely serving as a backing or support. In its preferred form, the container is formed of a multilayer material whose inner layer is formed of a plastic such as polyvinyl acetal e.g., polyvinyl butyral, polymeric esters such as cellulose acetate, cellulose acetate butyrate, polyvinyl acetate, polyvinyl chloride, etc. said layer being backed by a metal foil e.g., a lead foil or lead-tin foil which is impervious to the vapours of said solution. The containers may be strengthened by a more rigid backing material such as kraft paper or a plastic such as polyvinyl acetate and polyvinyl chloride. More details as to the construction of such a rupturable container can be found amongst others in U.S. Pat. 2,634,886 of Edwin H. Land, issued April 14, 1953.

The silver halide emulsion layer and/or the image-receiving layer may be coated on opaque or transparent supports. In this way it is possible to expose the

photosensitive element from either side as desired and it is possible to form either reflection prints or transparencies.

The image-receiving layer of the image-receiving element preferably comprises agents promoting precipitation of the silver from the transferred silver complex. Examples of such agents, called development nuclei or shortly nuclei, are well known and include sulphides, selenides, polysulphides, polyselenides, thioureas, thioacetamides, mercaptans, stannous halides, heavy metals or their salts and fogged silver halide. Sulphides of heavy metals such as of antimony, bismuth, cadmium, cobalt, lead, nickel and silver are also suited. Lead sulphide and zinc sulphide as well as the complex salts thereof are especially effective either in themselves or mixed with thioacetamide, dithiobiuret and dithio-oxamide. Among the heavy metals silver, gold, platinum, palladium and mercury are to be mentioned, preferably in colloidal form.

The development nuclei may be associated with a granular, inorganic, water-insoluble, substantially chemically inert substance such as silica as vehicle for the said nuclei whereby aggregation of the precipitated silver is promoted.

In at least one layer of the image-receiving element other substances may also be incorporated which play a part in the formation of the diffusion transfer image e.g. black-toning agents, anti-yellowing agents, optical bleaching agents, softening agents, etc.

For in-camera processing the image-receiving element may be constructed as described in U.S. Pat. 2,823,112 of Edwin H. Land, issued Feb. 11, 1958. According to this United States Patent Specification the print-receiving element is so constructed that the viscous processing fluid separates therefrom and leaves no droplets or film of developing composition on the print-receiving layer. The image-receiving layer is thin, holding a mass of water so small that there is no tactual wetness. Moreover, by making the print-receiving layer so thin the tendency to curl is also avoided. Consequently when peeled from the photosensitive element, which carries the viscous processing layer, the image-receiving element appears to be a dry sheet.

According to this United States Patent Specification a layer, which is substantially impervious to the processing liquid and which may be the liquid-impervious surface of a supporting sheet which is entirely formed of liquid-impervious material is provided between the silver precipitating layer in which the positive is formed, and the remainder of the image-receiving element. Further, the image-receiving layer is provided with a surface from which the viscous film of processing fluid may be readily stripped. Thus, according to said United States Patent Specification the outer surface of the image-receiving element contacting the layer of processing composition is so constituted as to have a lesser adhesion for the solid residue of the liquid processing composition than does the photosensitive element. As a result, the photosensitive element, when stripped from the image-receiving element, carries with it the residue of the processing composition. Further, between the image-receiving layer and the stripping layer an abrasion resistant coating may be provided.

According to this United States Patent Specification stripping of the silver halide element from the image-receiving element separates the layer of processing solution from the image-receiving element. However, as

noted hereinbefore in order to provide the image-receiving element with a protective coating, it is also possible that upon stripping the layer of processing solution remains in contact with the said image-receiving element. Such stripping techniques are taught in U.S. Pat. No. 2,647,056 of Edwin H. Land, issued July 28, 1953.

The following examples illustrate the present invention.

EXAMPLE 1

A photosensitive element was prepared which comprises a silver bromiodide emulsion layer applied to a paper support which layer contains per sq.m an amount of silver halide corresponding to 1.5 g of silver nitrate and 15 mg of compound 1. After exposure, the photosensitive element together with an image-receiving element comprising a silver receptive layer containing development nuclei which is coated on a water-impervious base, according to the practice described in U.S. Pat. No. 2,823,122 of Edwin H. Land, issued, Feb. 11, 1958, were advanced in superposed relationship between a pair of pressure applying rollers to spread between them in a thin layer a processing composition comprising per litre :

sodium carboxymethyl cellulose	40 g
sodium hydroxide	35 g
uracil	75 g
N,N-di(2-ethoxyethyl)-hydroxylamine	40 ml

After a contact period of 36 seconds, the emulsion together with the layer of processing liquid was stripped from the image-receiving element to uncover the positive print.

The print obtained was then placed in an atmosphere of 65° C and 100 percent relative humidity. After 1 hour the black image tone was still unaltered whereas when no compound of the invention was present in the silver halide emulsion layer, the image tone had changed to brown-black and brown.

The same favourable image-tone stabilizing effect was obtained when using in the silver halide emulsion layer instead of compound 1, 20 mg/sq.m of compound 4, 50 mg/sq.m of compound 5 and 20 mg/sq.m of compound 7.

EXAMPLE 2

Example 1 was repeated with the difference that the emulsion layer of the light-sensitive element did not contain a compound of the invention.

The positive print obtained after exposure of the light-sensitive element and further treatment as described in example 1 was then rubbed in with a solution of 100 mg of compound 6 in 100 ml of methanol.

After having been placed in an atmosphere of 65°C and 100 percent relative humidity for 1 hour the black image-tone of the print was found unaltered contrary to the image-tone of a print obtained under the same circumstances without the treatment with the solution of compound 6, which image-tone changed to brown.

We claim :

1. In a reproduction method according to the silver complex diffusion transfer process wherein an image-wise exposed silver halide emulsion layer of a light-sensitive element is developed and the non-developed and complexed silver halide from said emulsion layer is image-wise diffused into an image-receiving layer of

an image-receiving element where the complexed silver halide is converted into a silver containing image in the presence of development nuclei, the improvement of stabilizing the image-tone of the silver image in said image-receiving element which comprises either carrying out the diffusion transfer process in the presence of aromatic disulphide having at least one water-solubilizing carboxyl or sulfo group in acid or salt form or treating the image-receiving element subsequent to the formation therein of the silver complex diffusion transfer image with a solution of said disulphide.

2. Method according to claim 1 wherein said disulphide is present in at least one water-permeable layer of said light-sensitive element.

3. Method according to claim 1 wherein said disulphide is present in at least one water-permeable layer of said image-receiving element.

4. Method according to claim 1 wherein said disulphide is present in an aqueous solution with which said silver image is contacted after its formation.

5. Method according to claim 1 wherein said disulphide corresponds to the formula:



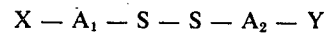
wherein:

each of A_1 and A_2 represents an arylene group, and each of X and Y represents a water-solubilizing carboxyl or sulfo group in acid or salt form, or a substituent carrying such water-solubilizing group in acid or salt form.

6. Method according to claim 5 wherein each of A_1 and A_2 stands for phenylene.

7. A photographic non-light-sensitive image-receiving element for use in a silver complex diffusion transfer process comprising in the image-receiving layer or in a layer in water-permeable relationship with said image-receiving layer an aromatic disulphide having at least one water-solubilizing carboxyl or sulfo group in acid or salt form.

8. An image-receiving element according to claim 26 wherein said disulphide corresponds to the formula:



wherein:

each of A_1 and A_2 represents an arylene group, and each of X and Y represents a water-solubilizing group in acid or salt form, or a substituent carrying such water-solubilizing group in acid or salt form.

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