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# STABILISATION OF DEVELOPED PHOTOGRAPHIC IMAGES

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## ABSTRACT OF THE DISCLOSURE

Exposed and developed photographic silver images can be stabilised by treating the layer containing the exposed image with a compound which reacts with the silver halide in the unexposed and undeveloped areas of the layer to form a light-insensitive reaction product. Fading of the silver images thus produced is prevented by performing the development in the presence of heterocyclic carboxyl-alkyl mercapto compounds.

Stabilisation of developed photographic images

The invention relates to a process for the production of photographic images by exposure, development and subsequent stabilisation, development being carried out in the presence of heterocyclic carboxyalkyl mercapto compounds which improve the stability of the silver image even after prolonged storage under extreme climatic conditions.

It is known to stabilise developed photographic images with complex forming compounds in rapid photographic reproduction processes as a substitute for conventional fixing with sodium thiosulfate followed by washing. In contrast to the method of fixing with sodium thiosulfate, in these stabilizing processes the silver salts remain in the unexposed and undeveloped parts of the layer in the form of a light-insensitive reaction product of the stabilising compound with the original silver halides. Stabilization of developed photographic materials has, however, certain disadvantages. One disadvantage is that nearly all substances which form complexes with silver halides attack metallic silver and hence the photographic image, converting the silver into a complex compound or simple silver salt. This leads to fading of the silver image or to a change in the color of the image silver from black to a brownish tone. This undesired effect occurs particularly in a moist atmosphere.

Fading of the black image area can be prevented by adding to the stabilising bath heterocyclic mercapto compounds such as 1-phenyl-5-mercaptotetrazole. However, the usual compounds of this type are only sparingly soluble in the acid stabiliser solutions so that it is difficult to apply a sufficient quantity of these compounds. They cannot be added in the required quantity to the emulsions because of their development inhibiting effect.

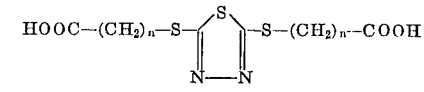
Fading of the black image areas can also be prevented by adding to the emulsion compounds which only decompose in alkaline solution to yield a mercapto compound. Such compounds, however, cannot be added to the emulsion in sufficient quantities to improve satisfactorily the keeping quality of the stabilised image on prolonged storage under extreme climatic conditions.

It is among the objects of the present invention to provide compounds which do not show the disadvantages referred to above, and which are stabilising black silver images particularly upon prolonged storage under extreme climatic conditions.

We now have found a process for the production of



photographic images including the steps of exposing a supported silver halide emulsion layer, developing and stabilising the exposed and developed layer wherein development is carried out with a bath which contains at least one heterocyclic compound of the following formulae:



wherein $n$ is 1 to 3.

Suitable compounds are summarized in the following table:

| Number | $n$ | M.P. in ° C. |
|---|---|---|
| 1 | 1 (disodium salt). | 286 (decomposition). |
| 2 | 2 | 145. |
| 3 | 3 | Oil. |

The preparation of these compounds is described in U.S. Patent No. 3,330,663.

For operating the process according to the invention, conventional light-sensitive photographic materials having at least one silver halide emulsion layer are suitable. The light-sensitive emulsions may contain any silver halides, such as silver chloride or silver bromide, if desired with a small proportion of silver iodide. Emulsions which have a high silver chloride content are preferred.

The binders for the light-sensitive layers may be the usual water-permeable layer-forming substances, particularly proteins, preferably gelatine.

Furthermore, the emulsions may contain alkylene oxide polymerisation products as chemical sensitizers. They may also contain the known stabilizers.

In addition, the emulsions may contain developers or developer combinations of the type hydroquinone, pyrocatechol, aminophenol, compounds of the pyrazolidone series, phenylene diamine derivatives and the like, antioxidants for the developer, e.g. potassium metalbisulfite, aldehyde and ketone bisulfite, matting agents and brightening agents.

Development is carried out in the usual manner, using known developers. According to a preferred method of carrying out the invention, the developer is added to the photographic material and development is initiated by treatment with an alkaline aqueous bath, hereinafter referred to as an activator bath.

The concentration of the compounds for use according to the invention in the development bath may vary within wide limits. The concentration depends upon the photographic material used and the nature of the developer. The optimum concentrations for a particular reproduction process can be determined by a few simple laboratory tests. Amounts of 0.5 to 10 g. per liter of treatment bath, preferably 1 to 5 g. per liter, have generally been found to be sufficient.

Suitable stabilising agents, i.e. compounds which are capable of converting the silver halide remaining after development into a compound which is not sensitive to light, have been described e.g. in British Patents Nos. 631,184 or 959,807 and in U.S. Patent No. 2,525,532 or French Patent No. 1,237,454. Ammonium thiocyanate, and alkali metal thiocyanates, e.g. sodium or potassium thiocyanate, have been found to be particularly suitable.

These stabilising baths may also contain the usual other additives such as alkali metal sulfites or metabisulfites or cycloalkanone bisulfites, acetic acid or its salts and organic compounds, particularly additional heterocyclic compounds which contain mercapto groups, such as 1-phenyl-5-mercaptotetrazole, which form sparingly soluble silver salts.

EXAMPLE 1

A light-sensitive photographic material comprising a supported silver chloride gelatin emulsion layer which emulsion layer contains 0.2 mol of silver halide with a silver iodide content of less than 0.1 mol percent of silver iodide per kg. of emulsion (amount of silver in the form of silver halide 1.3 g./m.$^2$) and hydroquinone (12 g. of hydroquinone per kg. of emulsion) is exposed to form an image and developed in the following activator solution:

50 g. of sodium hydroxide
40 g. of anhydrous sodium sulfite
2 g. of potassium bromide
1 g. of 1-phenylpyrazolidone-(3)

made up to 1 liter with water.

The compounds shown in the following table are added to the above activator solution. The quantities added are shown in the table.

The developed material is then treated with the following stabilising solution:

250 g. of ammonium thiocyanate
145 g. of potassium metabisulfite
100 ml. of a 3% aqueous solution of formaldehyde
25 ml. of 60% acetic acid,

made up to 1 liter with water.

The samples are processed in a two-bath development apparatus customarily employed. The treatment time is about 1 to 5 seconds in the activator bath and about 2 to 15 seconds in the stabilising bath.

To test the stability in storage of the silver image, a portion of the copy is kept over water in a vessel for 24 hours.

Several of these uniformly moist portions of the copy are inserted into a polyethylene container and this container is placed in a bag containing 30 ml. of water and sealed. The sealed containers are stored in a heating cupboard at 60° C. for 5, 24 and 48 hours, respectively, and the change of the silver image which has taken place after this time is examined.

Whereas the silver image of the copies produced according to the invention remains black or dark brown to black depending on the time of storage, under the above condition the comparison sample shows discoloration varying from brown to pale brown. The maximum density of



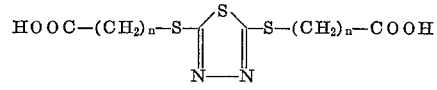
the various fresh, air-dried materials and those which have been stored in moist heat is measured in a densitometer. The following results are obtained:

TABLE

| Compound added No. | Concentration, g./l. | Air dried | Maximum density after storage in moist heat for— 5 hours | 24 hours | 48 hours |
|---|---|---|---|---|---|
| Control sample | | 1.46 | 1.08 | 0.35 | 0.28 |
| 1 | 15 | 1.42 | 1.30 | 0.89 | 0.68 |
| 2 | 5 | 1.40 | 1.32 | 1.09 | 0.93 |
| 3 | 5 | 1.41 | 1.36 | 1.08 | 0.89 |

We claim:

**1.** A process for the production of photographic images by exposure of a photographic material which has at least one silver halide emulsion layer, development and stabilisation of the unexposed and undeveloped silver halide, wherein development is performed with a bath containing at least one compound of the following formula or salts thereof:



in which *n* denotes 1–3.

**2.** The process of claim **1**, wherein the photographic material contains in the light-sensitive silver halide emulsion layer a photographic developer substance and wherein development is performed with an aqueous alkaline bath.

**3.** The process of claim **1**, wherein the stabilizer bath contains ammonium thiocyanate as stabilising agent.

**4.** The process of claim **3**, wherein the stabilising bath in addition contains cyclohexanone bisulfite.

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U.S. Cl. X.R.

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