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PHOTOGRAPHIC MATERIAL

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No Drawing. Continuation-in-part of abandoned application Ser. No. 49,993, June 25, 1970. This application Oct. 12, 1971, Ser. No. 188,464
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Int. Cl. G03c 1/06, 1/48, 5/30
U.S. Cl. 96—66.3 5 Claims

ABSTRACT OF THE DISCLOSURE

This application describes a process for the production of developed photographic material which comprises subjecting photographic lith material containing a latent silver image in a silver halide emulsion layer to development by means of a formaldehyde/bisulphite/hydroquinone lithographic developer, the process being characterized in that the development takes place in the presence of a water-soluble polyethylene oxide chain $\{CH_2CH_2O\}_n$ where n is an integer from 5–200 and an organic mercapto compound selected from dialkyl substituted thioureas and heterocyclic nitrogen compounds containing a mercapto group attached to a carbon atom which is in the alpha position with respect to a nitrogen atom in the heterocyclic ring.

This application is a continuation-in-part of my application Ser. No. 49,993 entitled "Photographic Material," filed June 25, 1970, now abandoned.

This invention relates to the processing of photographic light-sensitive materials intended for use in recording halftone dot images or line images and which carry a gelatin silver halide emulsion of very high contrast characteristics.

Photographic light-sensitive materials of the above type are designed to be developed in formaldehyde-containing low-sulphite hydroquinone deevelopers and when so developed the phenonmenon known as infectious development occurs.

Emulsions of the foregoing type (which are herein referred to as "lith" emulsions) may be developed satisfactorily over a considerable range of development times, other development conditions being held constant. The effective "speed" of the lith emulsions increases as the development time is increased; this is the infectious development referred to above and accordingly it is a valuable property of such materials that by controlling development time it is possible to control the effective emulsion speed.

It is, however, important in such lith materials that the contrast of the resulting images should remain high over as large a range of development times as possible and it is known to achieve this by the addition of polyethylene oxide compounds to the photographic emulsion or developer so that normal formaldehyde/bisulphite/hydroquinone developer solution can be used, i.e. so that infectious development can take place. (It is to be noted that accordingly the polyethylene oxide compounds act in no way as emulsion sensitisers nor do they enhance the speed of development of the exposed material.)

This system works well when the actual length of development time is not a factor which needs to be considered but in recent years there has been an increasing tendency for lith material to be machine processed. With a machine processing technique it is desirable to speed up the processing time while retaining the high contrast and infectious development features of the lith process. It is possible to speed up the processing time by omitting the polyethylene oxide condensate for either the emulsion

or the developing solution or by reducing its concentration. However this means a considerable diminution in the desirable high contrast obtained in the developed material.

It is the object of the present invention to provide a method of processing lith material in a formaldehyde/bisulphite/hydroquinone developer in the presence of a polyethylene oxide condensate wherein the speed of development is increased without any concomitant decrease in the contrast of the developed image.

According to the present invention, therefore, there is provided a process for the production of developed photographic material which comprises subjecting photographic lith material containing a latent silver image in a silver halide emulsion layer to development by means of a lithographic developer of the formaldehyde/bisulphite/hydroquinone type, the development taking place in the presence of a water-soluble polyethylene oxide condensate which is a compound which comprises a polyethylene oxide chain $\{CH_2CH_2O\}_n$ where n is an integer from 5–200, and an organic mercapto compound selected from dialkyl substituted thioureas, and heterocyclic nitrogen compounds containing a mercapto group attached to a carbon atom which is in the alpha position with respect to a nitrogen atom in the heterocyclic ring.

By use of the process of present invention there is achieved an enhanced speed of development without any concomitant decrease in the contrast of the developed image. This is surprising because the dialkyl substituted thioureas of use in the present invention are not known to exhibit any effect when present in a photographic emulsion whilst the heterocyclic nitrogen compounds containing a mercapto group attached to a carbon atom which is in the alpha position with respect to a nitrogen atom in the heterocyclic ring find use as emulsion stabilisers. Thus none of the organic mercapto compounds of use in the present invention are emulsion sensitisers and therefore it is unexpected that the presence of such compounds during the development stage of lithographic material in the presence of polyethylene oxide condensates should lead to the desirable results obtained.

It is preferred that both the polyethylene oxied condensate and the organic mercapto compound are present initially in the photographic lith material either in the emulsion layer thereof or in the supercoat layer.

By "lithographic developer of the formaldehyde/bisulphite/hydroquinone type" is meant a developer system containing hydroquinone only as developing agent but with sulphite ion present as a formaldehyde bisulphite complex with an addition of up to 1% by weight of free sodium sulphite. The pH of the developer is maintained at values between 9.8–10.5. This formulation enhances infectious type development resulting in extremely high contrast of lith type emulsions.

By "photographic lith material" is meant photographic high contrast material which comprises a fine grain high contrast silver halide emulsion in which the halide generally comprises at least 50 mole percent chloride and less than 5 mole percent iodide, the remainder being bromide.

The emulsion may be sensitised with gold salts and/or sulphur containing compounds such as thiosulphate or it may be reduction sensitised. The emulsion may also be optically sensitised and contain stablising agents for example tetrazindines.

By polyethylene oxide condensate is meant any polymeric compound which comprises a polyethylene oxide chain of the type $\{CH_2—CH_2—O\}_n$ where n is from 5–200. Such compounds include polyethylene glycol and condensation products of ethylene oxide with, for example, aliphatic alcohols, saturated aliphatic acids, alkyl substituted phenols and hexitol rings. Such compounds also

include block copolymers of ethylene oxide with, for example, polypropylene oxide.

Preferably the polyethylene oxide condensate is present, as hereinbefore stated, in the photographic emulsion and when so present the preferred amount is 0.02 to 3 g. per g. mole of silver in the emulsion. However the polyethylene oxide condensate may be present in the lithographic developer and when so present the preferred concentration is 0.05–3.0 g. per litre.

Preferably the organic mercapto compound is present, as hereinbefore stated in the photographic emulsion and when so present the preferred amount is 0.001 to 0.1 g. per g. mol of silver present in the emulsion. The organic mercapto compound may be added to the emulsion at any stage before coating the emulsion on to the support. However the organic mercapto compound may be present in the lithographic developer and when so present the preferred concentration is 0.00001 to 0.001 g. per litre of developing solution.

An example of a dialkyl substituted thiourea is N,N' dibutyl thiourea.

Examples of heterocyclic nitrogen compounds containing a mercapto group attached to a carbon atom which is in the alpha position with respect to a nitrogen atom in the heterocyclic ring particularly suitable for use in the process of the present invention are ethylene thiourea, 1 - methyl - 5 - mercapto-1,2,3,4-tetrazole, 4,5-dimethyl-3 - mercapto - 1,2,4 - triazole, 7-hydroxy-2-mercapto-5-methyl-1,3,3α,7-tetraazindene, rhodanine, thiazolidene-2-thione, thiohydantoin, oxazolidine-2-thione.

The preferred compound of these is 1-methyl-5-mercapto-1,2,3,4-tetrazole.

The following Examples will serve to illustrate the invention.

EXAMPLE 1

Emulsion I

A gelatin silver chlorobromide emulsion containing 31% silver bromide having a mean grain diameter of 0.4 was sulphur sensitised, stabilised and treated with an orthochromatic sensitising dye. 0.3 g. per gram mol of silver of a polyethylene oxide condensate (a cetyl alcohol condensate with 23 ethylene oxide units) was added after chemical sensitisation. The emulsion was then coated on a lithographic film base with a suitable antihalation backing.

Emulsion II

A similar emulsion was treated in the same manner except that 17 milligrams of 4,5-dimethyl-3-mercapto-1,2,4-triazole per gram mole silver was added after chemical sensitisation.

Emulsion III

A similar emulsion as described for Emulsion I was treated in the same manner except that 7 milligrams of 1-methyl-5-mercapto-1,2,3,4-tetrazole per gram mol silver was added after chemical sensitisation.

Emulsions IV–VIII

Similar emulsions as described for Emulsions II and III were treated in a similar manner but the additions of development accelerator were as follows:

Emulsion:

IV 33 milligram 7-hydroxy-2-mercapto-5-methyl-1,3,3α,7-tetraazindene
V 20 milligram N,N'-dibutyl thiourea
VI 1.7 milligram thiohydantoin
VII 3.3 milligram oxazolidine-2-thione
VIII 1.7 milligram ethylene thiourea.

The coated emulsions were exposed behind an optical wedge in the usual manner. The exposed coatings were then developed in solutions of the following formulation:

Solution A:	Gr.
Sodium sulphite (cryst.)	120
Hydroquinone	45
Boric acid	15
Potassium bromide	3.15
Water to make 1,500 ml.	

Solution B:	Gr.
Paraformaldehyde	15
Potassium metabisulphite	5.25
Sodium sulphite (cryst.)	1.05
Water to make 500 ml.	

The developer is made by mixing 3 parts of Solution A with one part of Solution B immediately before use. The following sensitometric results were obtained with the test coatings.

TABLE 1

Emulsion	Development time at 68° F.	Relative log speed	Contrast $\overline{G}$ 0.1–2.1
I	2½	2.62	5.5
	3½	2.90	11
II	2½	2.91	8.5
	3½	3.18	16
III	2½	2.86	10
	3½	3.05	12
IV	2½	2.87	7.5
	3½	3.12	7.5
V	2½	2.84	12
	3½	3.04	10
VI	2½	3.00	9.0
	3½	3.15	7.8
VII	2½	2.87	12
	3½	2.99	7.0
VIII	2½	2.92	13
	3½	3.01	8.5

The above Table illustrates the increased development rate associated with the speed gain and without loss in lithographic properties, by the addition of certain organic mercapto compounds to the emulsion.

The contrast values stated in the above Table 1 and Table 2 which follows are expressed as $\overline{G}$ 0.1–2.1. This is defined as the slope of the straight line joining points of speed values between S 0.1 and S 2.1 above the basic fog level of the developed film.

EXAMPLE 2

An emulsion was prepared as in Example 1 (Emulsion I) and exposed in the usual manner. The exposed coatings were then developed in the formulation specified but with the addition of one of the selected compounds as follows:

TABLE 2

Developer	Selected compound	Quantity, mgrms./l. developer (working strength)	2½ min. development		3½ min. development	
			Relative log speed	Contrast $\overline{G}$ 0.1–2.1	Relative log speed	Contrast $\overline{G}$ 0.1–2.1
I	0	0	2.60	4.5	3.14	10
II	4,5-dimethyl-3-mercapto-1,2,4-triazole	0.1	2.78	5.2	3.24	7.0
III	7-hydroxy-2-mercapto-5-methyl-1,3,3σ,9-tetraazindene	0.1	2.86	4.7	3.24	8.0
IV	Thiazolidine-2-thione	0.05	2.80	4.9	3.20	8.5
V	N,N'-dibutyl thiourea	0.1	2.92	7.0	3.26	8.5

Results in Table 2 show that the advantages of increased development rate with no significant loss in contrast, with lithographic emulsions containing polyethylene oxide condensate may be obtained by addition to the developer of certain organic mercapto compounds as hereinbefore defined.

I claim as my invention:

1. A process for the production of developed photographic material which comprises subjecting photographic lith material containing a latent silver image in a silver halide emulsion layer to development by means of a formaldehyde/bisulphite/hydroquinone lithographic developer, the process being characterized in that the development takes place in the presence of a water-soluble polyethylene oxide condensate which is a compound which comprises a polyethylene oxide chain

$$\text{-}CH_2CH_2O\text{-}_n$$

where n is an integer from 5–200 and a heterocyclic nitrogen compound selected from the group consisting of ethylene thiourea, 1-methyl-5-mercapto-1,2,3,4-tetrazole, 4,5-dimethyl-3-mercapto-1,2,4-triazole, 7-hydroxy-2-mercapto - 5 - methyl-1,3,3α,7-tetraazindene, rhodanine, thiazolidene - 2 - thione, thiohydantoin and oxazolidine - 2-thione.

2. A process according to claim 1 wherein both the polyethylene oxide condensate and the heterocyclic nitrogen compound are present initially in the photographic lith material in the emulsion layer thereof or in the supercoat layer.

3. A process according to claim 2 wherein from 0.02 to 3 g. of the polyethylene oxide condensate per g. mole of silver in the emulsion is present in the emulsion.

4. A process according to claim 2 wherein from 0.001 to 0.1 g. of the heterocyclic nitrogen compound per g. mole of the silver in the emulsion is present in the emulsion.

5. A process for the production of developed photographic material which comprises subjecting photographic lith material containing a latent silver image in a silver halide emulsion layer to development by means of a formaldehyde/bisulphite/hydroquinone lithographic developer, the process being characterized in that the development takes place in the present of a water-soluble polyethylene oxide condensate which is a compound which comprises a polyethylene oxide chain $\text{-}CH_2CH_2O\text{-}_n$ where n is an integer from 5–200 and 1-methyl-5-mercapto-1,2,3,4-tetrazole.

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