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3,701,662  
**COLOR PHOTOGRAPHIC PROCESS USING  
A BLEACH-FIX SOLUTION CONTAINING  
A METAL COMPLEX OF A SELENIUM  
COMPOUND**  
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1,617/70  
Int. Cl. G03c 7/00  
U.S. Cl. 96—55 9 Claims

### ABSTRACT OF THE DISCLOSURE

This application describes a colour development process for colour silver halide photographic material, wherein the material after development is treated with a bleach-fix solution which contains a mild oxidising agent, a silver halide solvent and as a bleach-fix accelerator a water-soluble complex consisting of a specified metal and selenourea, a specified N-alkyl substituted selenourea or a specified selenosemicarbazide.

This invention relates to the processing of photographic material comprising silver halide emulsion layers to yield material having colour dye images therein.

In the processing of conventional colour photographic material a developable silver salt image is developed with an aromatic primary amino developing agent of the para-phenylene diamine type (a so-called "colour developer") in the presence of a compound (a so-called "colour coupler") which will combine with the oxidation products of the colour developer to form an azomethine or quinone-imine dye. The dye is thus formed in situ with the developed silver image. Subsequently the product must be treated with a bleach bath and a fixing bath or a combined bleach-fix bath thereby to remove silver and any residual silver halide or other silver salt, leaving in the product only the dye image.

In the silver-dye bleach process of colour photography the photographic material comprises at least one silver halide emulsion layer which includes as a dispersion therein an organic dyestuff or the type which can be destroyed (or bleached) by finely divided silver in a suitable treatment bath. The organic dyestuff is usually an azo dye. Most commonly three such silver halide emulsion layers are present, each of which is sensitive to a different region of the visible spectrum and each of which contains a different azo dye. The usual processing sequence for the production of a dye image in the material is after an image-wise exposure to develop the material in a black and white developer. The development is then stopped and the unexposed silver halide is fixed out. Then after washing the material is treated in a dye-bleach bath which oxidises the silver image and simultaneously reduces (bleaches) the dye in the region of the silver image. The silver salts and any residual silver must then be removed. This is usually accomplished by washing the material after its treatment in the dye-bleach bath and then treating it in a bleach bath followed by a fixing bath or treating it in a combined bleach-fix bath. The photographic material then contains a dye image only; this dye image being usually a direct positive reproduction of the original.

In one commercially available silver-dye-bleach material the amount of residual silver left after the dye-bleach

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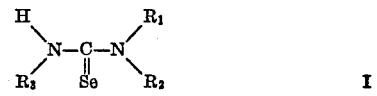
step is not negligible because this material requires to be processed so that the dye-bleach step is terminated before all the image silver has been used in reducing the dye. Thus in the processing of this silver-dye-bleach material in particular it is essential that an effective silver bleach step succeeds the dye-bleach step in order to ensure that the residual silver is removed as completely as possible from the material.

In both the processing of conventional colour photographic material and in the processing of silver-dye-bleach material the use of a combined bleach-fix bath is preferable because it results in a reduction of the processing time and of the cost of processing equipment required. Normally a bleach-fix bath comprises a mild oxidising agent for example a ferric chelate complex, a cupric complex a salt or a cobalt (III) complex together with a silver halide solvent or fixing agent for example a water-soluble thiosulphate or a water-soluble thiocyanate. Strong oxidising agents cannot be used because they tend to oxidise the silver halide solvent.

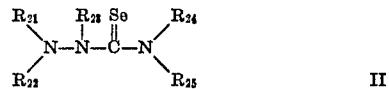
Stable bleach-fix solutions comprising ferric chelate complexes and sodium thiosulphate may be obtained but because of the weak oxidising power of the ferric chelate complex such bleach-fix baths can only be used commercially for the processing of photographic materials with a fairly low silver content.

It has been proposed to use selenourea, certain N-alkyl substituted selenoureas and certain substituted seleno-semicarbazides as bleach-fix accelerators in a bleach-fix step which can be used in the processing of colour photographic material which have a relatively high silver content, for example colour negative material and colour reversal material. It has now been found that certain metal complexes of these compounds may be used instead of the compounds as bleach-fix accelerators.

According to the present invention in the processing of colour photographic material comprising silver halide emulsion layers to yield material having colour dye images therein there is provided a bleach-fix step which comprises treating the photographic material with a stable bleach-fix bath which comprises an aqueous solution of a mild oxidising agent and a silver halide solvent which is either a water-soluble thiosulphate or a water-soluble thiocyanate in the presence of a bleach-fix accelerator which comprises a water-soluble complex consisting of a metal selected from iron, cobalt, nickel, copper, zinc, palladium, silver, cadmium, indium, tin, antimony, platinum, gold, mercury, lead and bismuth and (a) selenourea, (b) an N-alkyl substituted selenourea of the general Formula I:



wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are hydrogen atoms or alkyl groups, at least one of them being a hydrogen atom, or (c) a selenosemicarbazide of the general Formula II:



wherein one of  $\text{R}_{21}$  and  $\text{R}_{22}$  is a hydrogen atom or an alkyl, aralkyl or aryl group and the other of  $\text{R}_{21}$  and  $\text{R}_{22}$  is a hydrogen atom or an alkyl group,  $\text{R}_{23}$  is a hydrogen atom or an alkyl, aralkyl or aryl group, one of  $\text{R}_{24}$  and  $\text{R}_{25}$  is a hydrogen atom or an alkyl, aralkyl or aryl group

and the other of  $R_{24}$  and  $R_{25}$  is a hydrogen atom or an alkyl group but at least one of  $R_{23}$ ,  $R_{24}$  or  $R_{25}$  being a hydrogen atom and there being not more than one group selected from aryl and aralkyl present in the compound.

By "stable bleach-fix bath which comprises an aqueous solution of a mild oxidising agent and a silver halide solvent" is meant a bleach-fix bath wherein the oxidising agent is strong enough to bleach the silver but is not strong enough to oxidise the silver halide solvent, i.e. the thiocyanate or the thiosulphate, to an appreciable degree.

The preferred mild oxidising agents for use in the present invention are ferric chelate complexes or diaquo-tetramine-cobalt (III) complexes.

By ferric chelate complex is meant a co-ordination compound of the ferric ion and a compound which comprises nitrogen and/or oxygen-containing co-ordinating groups. The most important co-ordinating groups are amino, heterocyclic nitrogen, carboxyl and carbonyl groups.

The preferred ferric chelate complex for use in the bleach-fix step of the present invention is a ferric ethylenediaminetetraacetic acid complex. It is to be understood that this compound may be used as such in the preparation of a bleach-fix bath or it may be formed in situ in a bleach-fix bath by ethylenediaminetetraacetic acid reacting with a ferric salt, e.g. ferric chloride. In Example I which follows the ferric ethylenediaminetetraacetic acid complex has been formed in situ.

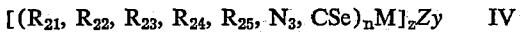
Other ferric chelate complexes which may be used in the present invention are for example pyridine-2:6 dicarboxylateferrate (III) complex, iminodiacetatoferate (III) complex and nitrilo-triacetate-ferrate (III) complex.

It is thought that the selenourea-metal complexes of use in the present invention as bleach-fix accelerators have the general Formula III:



wherein  $R_1$ ,  $R_2$ ,  $R_3$  are each hydrogen atoms or alkyl groups, at least one of them being a hydrogen atom,  $M$  is one of the metals in the list hereinbefore set forth,  $Z$  is an anion,  $z$  is the valency of the anion and  $y$  is the valency of the complex cation.

It is thought that the selenourea-metal complexes of Formula II-metal complexes of use in the present invention as bleach-fix accelerators have the general Formula IV:

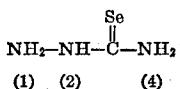


where  $M$ ,  $Z$ ,  $y$  and  $z$  have the meanings assigned to them above and  $n$  is 1 or 2 and  $R_{21}$ - $R_{25}$  have the meanings assigned to them in Formula II.

The preparation of metal-complex salts of selenourea and silver, copper, mercury, lead and cadmium ions has been described by M. A. Verneuil in *Annales de Chimie et de Physique*, Ser. 6, 9, 289 (1886) by H. Schmidt in *Med. Chem. Abhandl. med-chim Forschungstatten*, I. G. Farbenind., 3, 418 (1936) and by N. N. Po Proskina, S. M. Chul'skaya, G. F. Volodina, A. V. Ablov, Shur. *Strukt. Khim.*, 9, 1095 (1968).

The selenoureas of the above Formula III are known compounds as shown by the references set forth below.

The following Formula VI indicates the nitrogen atom referred to in the references.



4-phenylselenoureas—preparation described by Jensen & Frederiksen, *Z. anorg allgem Chem* 230 31-3 (1936)

2-phenylselenoureas—preparation described by Mautner & Kumler, *J. Amer Chem Soc* 97-101 (1956)

4-ethylselenoureas—preparation described by Huls & Renson, *Bull soc chim Belges* 65 684-95 (1956)

5 4-propylselenoureas—preparation described by M. Colland-Charon, Huls & Renson, *Bull soc chim Belges* 71 541-53 (1962)

1-phenylselenoureas and

1-(p-tolyl) selenoureas—preparations described by Colland-Charon, Juls & Renson, *Bull soc chim Belges* 71 554-62 (1962)

2-methylselenoureas,

4-methylselenoureas,

1,1-dimethylselenoureas,

1,2-dimethylselenoureas and

1,2,4-trimethylselenoureas—preparations described by Jensen, Felbert, Pedersen & Svanholm, *Acta chem Scand* 20(1) 278-81 (1966)

2-methyl-4-phenylselenoureas,

4-(p-chlorophenyl)selenoureas and

4-(p-methoxyphenyl)selenoureas—preparations described by Bulka, Ahlens & Tucek, *Chem Ber.* 100 (4) 1373-8 (1967)

25 The bleach-fix accelerators of use in the present invention are preferably added to the bleach-fix bath but they may be present during the bleach-fixing treatment adsorbed to or absorbed in the colour photographic material. In the processing of conventional colour photographic material,

30 such baths are stop baths and stop-fix baths. The bleach-fix step. Exemplary of such baths are stop baths and stop-fix baths. The bleach-fix accelerators should not be present, however, in the developing solution as they interfere with the development of the colour material. For

35 the same reason the bleach-fix accelerators of use in the present invention should not be present initially in the photographic material.

In the processing of silver-dye-bleach material the bleach-fix accelerators may be present in the wash bath which succeeds the dye-bleach treatment bath and precedes the bleach-fix bath but the bleach-fix accelerators should not be present during the dye-bleach treatment as they can interfere with this treatment step. Thus the bleach-fix accelerators should not be present initially in the silver-dye-bleach photographic material.

A number of the bleach-fix accelerators of use in the present invention as hereinbefore defined are not soluble in water unless the water comprises a thiosulphate. Thus preferably the bleach-fix accelerators of use in the present invention are added to a bleach-fix bath which comprises thiosulphate or to a stop-fix bath which comprises thiosulphate.

According to another embodiment of the present invention there is provided a stable bleach-fix bath which comprises an aqueous solution of a mild oxidising agent, as hereinbefore defined, a water-soluble thiosulphate and a bleach-fix accelerator which is either a selenoureas—metal complex as hereinbefore defined or a selenoureas—metal complex as hereinbefore defined.

60 Preferably in this aspect of the invention the mild oxidising agent is a ferric chelate complex or a diaquo-tetramine-cobalt (III) complex.

It is preferred that the concentration of selenoureas—metal complex or selenoureas—metal complex present in the bleach-fix bath is greater than 1 mg. per litre of bleach-fix bath. The most preferred amount being 150 mg. of bleach-fix accelerator per litre of bleach-fix bath.

70 It is preferred that the concentration of selenoureas—metal complex or selenoureas—metal complex present

in the stop-fix bath, stop bath or in a wash bath, is greater than 1 mg. per litre of the solution.

The selenourea-metal complexes of use in the present invention are more resistant to air oxidation and photochemical decomposition than the selenoureas from which they are prepared. The metal-complex compounds may be stored under normal conditions and dry-packed with only a minimum risk of the compounds deteriorating. On the other hand selenoureas stored under normal conditions or dry-packed soon turn first pink and then black probably due to a breakdown of the compounds with formation of elemental selenium. For example a sample of pure selenourea, obtained by recrystallisation from methanol in the dark, stored in a stoppered glass bottle and kept under normal laboratory conditions, turned black and showed a decomposition of about 15% after 20 days. While samples of (selenourea)<sub>2</sub>AgCl complex, (selenourea)<sub>2</sub>SbCl<sub>3</sub> complex, (selenourea)<sub>2</sub>SnCl<sub>2</sub> complex and (selenourea)<sub>2</sub>BiCl<sub>3</sub> complex kept under the same conditions for the same time showed no analytically detectable decomposition.

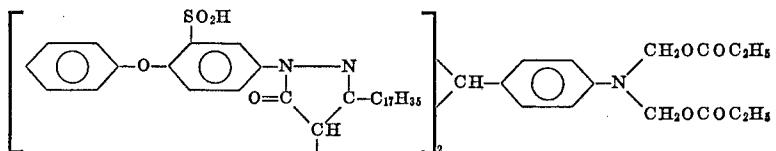
Selenosemicarbazide metal complexes offer similar advantages.

The following preparation of a complex of selenourea-silver thiosulphate is illustrative of the general method of preparation of the metal complexes of use in the present invention as bleach-fix accelerators.

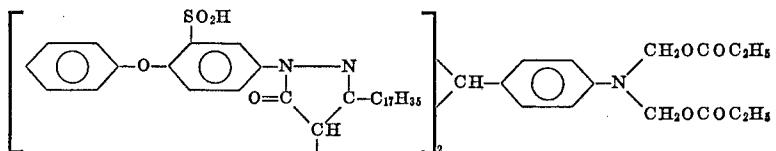
#### Preparation

A solution containing boric acid (22.5 g.), borax (12.5 g.), sodium thiosulphate pentahydrate (95.0 g.), water to 1 litre was prepared (Solution A). The pH of this solution was 7.04.

Silver nitrate (0.0060 moles) was dissolved in 10 ml. of water. Sodium hydrogen carbonate (1.0 g.) was added



the green sensitive layers each contained a magenta colour coupler of the formula:



the red sensitive layers each contained a cyan colour coupler of the formula:



to this solution. It produced evolution of carbon dioxide and a yellow precipitate. 25 ml. of Solution A was added to the suspension and the resulting mixture was again a clear solution (Solution B).

Selenourea (0.0060 moles) was dissolved in 50 ml. of Solution A and the resulting solution was added to Solution B. The white precipitate obtained was filtered, washed with water and then with methanol and dried under reduced pressure. Analytical results indicated the formula:



The selenourea-metal complexes may be prepared as follows.

A given volume of a 0.1 molar solution of the metal salt is prepared by dissolving the required quantity of metal salt in water or in a relatively strong acid solution. (An acid solution is necessary when salts of easily hydrolysed metal ions are involved, e.g. bismuth and antimony). This solution of the metal salt is added to a volume of 0.3 molar solution of the selenourea in 2 normal acid. The volume of the selenourea solution used is such that the molar ratio between the selenourea and the metal ion should be slightly greater than 2. This addition is carried out at 40° C. and, in the case of easily oxidised metals, all the preparation should be carried out under nitrogen. The complex salt precipitates soon or a few minutes after cooling.

The selenosemicarbazide metal complex, i.e. the complexes formed between the list of metals hereinbefore set forth and the compound of Formula II, may be prepared similarly except that the molar ratio between the selenosemicarbazide and the metal ion may be greater than 1.

The following example will serve to illustrate the use of a selenourea-metal complex as a bleach-fix accelerator.

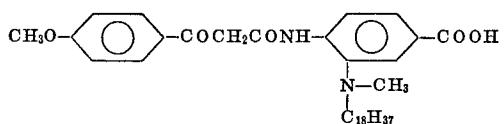
#### EXAMPLE I

5 Samples from a batch of a colour negative tripack material of the colour coupler substantive type containing 73.6 mg. of silver per dm.<sup>2</sup> as silver iodobromide emulsion were fogged and processed at 24° C.

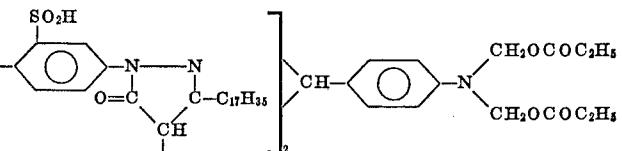
Details of the colour film used are as follows:

10	Layer order and sensitivity	Silver coating weight in mg. of Ag/dicemetre <sup>2</sup>
15	Non Stress	13.4
	Blue sensitive	13.4
	Colloidal silver filler layer	13.1
20	Green sensitive topcoat	13.1
	Intralayer	16.0
	Green sensitive subcoat	16.0
	Interlayer	17.5
25	Red sensitive topcoat	13.6
	Red sensitive subcoat	13.6
	Base of cellulose triacetate	
	Total	73.6

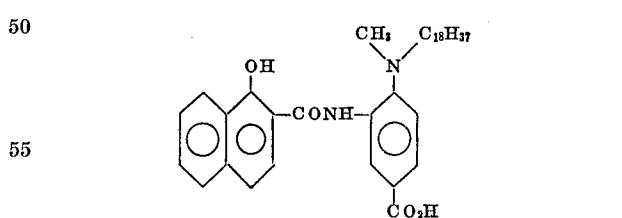
25 In this film: the blue sensitive layer contained a yellow colour coupler of the formula:



the green sensitive layers each contained a magenta colour coupler of the formula:



the red sensitive layers each contained a cyan colour coupler of the formula:



The processing sequence was:

65	Colour development: 6 minutes	
	Sodium metabroate	g 53.3
	Sodium hydroxide	g 2.0
	Sodium sulphite anhydrous	g 3.9
	Potassium bromide	g 0.70
	Hydroxylamine sulphate	g 2.34
	Sodium sulphate anhydrous	g 7.8
70	4-amino-N-ethyl-N-(4-hydroxybutyl) - aniline sulphate	g 6.0
	Water to 1 litre.	
75	pH 10.5.	

Stop-fix: 4 minutes

Sodium thiosulphate pentahydrate	g	171.0
Sodium acetate anhydrous	g	31.4
Sodium sulphite anhydrous	g	4.3
Acetic acid (glacial)	ml	35
Potassium alum	g	17.0
Ammonium chloride	g	43.0

Water to 1 litre.

pH 4.3.

Wash: 4 minutes

Bleach-fix: 6 minutes

Disodium tetraborate decahydrate	g	12.5
Boric acid	g	22.5
Sodium hydroxide	g	10.0
Ethylene diaminetetraacetic acid	g	16.2
Disodium salt of ethylenediaminetetraacetic acid dihydrate	g	3.5
Ferric chloride (60% w/v. soln)	ml	15
Sodium thiosulphate pentahydrate	g	95.0
Sodium sulphite anhydrous	g	4.0
Magnesium sulphate	g	20

Water to 1 litre.

pH 7.0.

Wash: 4 minutes

Conditioner: 4 minutes

Disodium salt of ethylenediaminetetraacetic acid dihydrate	g	0.50
Sodium carbonate anhydrous	g	4.5
Formaldehyde (40% w/v. soln)	ml	10
Lissapol N (8% soln)	ml	1.7

Water to 1 litre.

pH 10.7.

Wash: 4 minutes

After processing the remaining samples were analysed and were found to contain 13.84 mg. of metallic silver per square decimetre. Other samples of the same negative material were fogged and processed as above but bleach fixed for 12 minutes, after processing they were found to contain 9.81 mg. of metallic silver per square decimeter. These results were used as a control for a series of tests wherein samples of the same negative material were fogged and processed as above except that in Series A selenourea-silver chloride complex was added to the stop-fix bath and in the Series B selenourea-silver chloride complex was added to the bleach-fix bath.

The effect of the addition of these bleach-fix accelerators to the bleach-fix bath and to the stop-fix bath is shown in Table I below wherein the amount of residual metallic silver in the negative material after processing is given. The values refer to bleach-fixing times of 6 and 12 minutes.

TABLE I

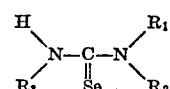
Accelerator used	Bath to which the accelerator was added	Concentration of the accelerator (mg./litre)	Residual silver after	
			6' bleach fixing (mg./dm. <sup>2</sup> )	12' bleach fixing (mg./dm. <sup>2</sup> )
Control			13.84	9.81
Series A (selenourea) $\text{AgCl}$	Stop-fix	400	0.81	0.54
Series B (selenourea) $\text{AgCl}$	Bleach-fix	150	0.86	0.36

A great reduction in the amount of residual silver in the samples which were processed a bleach-fix bath which comprises the bleach-fix accelerator (Series B) is thus shown. Also shown is the great reduction in the amount of residual silver in the samples of Series A which had been bleach-fixed in the presence of the bleach-fix accelerator, in this case the accelerators were present absorbed in the film material and were derived from the stop-fix bath to which they had been added.

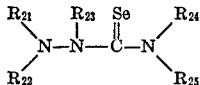
## 8 EXAMPLE II

A positive tripack colour material intended for the silver dye-bleach system comprising silver halide emulsions containing bleachable azo-dyes "Cibachrome" manufactured by Ciba Geigy A.G. of Switzerland was given a neutral wedge exposure and processed, the processing sequence being as follows:

10	Development: 10 minutes	
	p-Methyl-aminophenol-sulphate	g
	Sodium sulphite anhydrous	g
	Hydroquinone	g
	Sodium carbonate anhydrous	g
	Potassium bromide	g
	Water to 1 litre.	
	Stopfix: 4 minutes	
	Sodium thiosulphate pentahydrate	g
	Sodium sulphite anhydrous	g
	Water to 1 litre.	
	Wash: 8 minutes	
	Dye-bleach: 20 minutes	
	Sulphuric acid, 96%	ml
25	Potassium iodide	g
	Solution of 0.3 g. 2,3-dimethyl-6-aminoquinoxaline in 50 ml. ethanol	ml
	Water to 1 litre.	
	Wash: 4 minutes	
	Bleach-fix: 6 minutes	
	Disodium tetraborate decahydrate	g
	Boric acid	g
	Sodium hydroxide	g
	Ethylenediaminetetraacetic acid	g
	Disodium salt of ethylenediaminetetraacetic acid dihydrate	g
	Ferric chloride (60% w/v. soln)	ml
40	Sodium thiosulphate pentahydrate	g
	Sodium sulphite anhydrous	g
	(Selenourea) <sub>2</sub> AgCl	mg
	Water to 1 litre.	
	Wash: 8 minutes	
	Dry	
45	The processed material was satisfactory and substantially no residual silver was left in the material even in the areas of high exposure. Similar silver-dye-bleach material was exposed and processed using the same solutions as set forth above except that the bleach-fix solution contained no selenourea-silver complex. Even when the material had been treated in the bleach-fix bath for 25 minutes it was unsatisfactory because it had a high minimal density due to the incomplete removal of the residual silver in the areas of high exposure.	
	I claim as my invention:	
55	1. In the processing of colour photographic material comprising silver halide emulsion layers to yield material having colour dye images therein the bleach-fix step which comprises treating the photographic material with a stable bleach-fix bath which comprises an aqueous solution of a mild oxidising agent and a silver halide solvent which is either a water-soluble thiosulphate or a water-soluble thiocyanate in the presence of a solution of a bleach-fix accelerator which comprises a complex consisting of a metal selected from iron, cobalt, nickel, copper, zinc, palladium, silver, cadmium, indium, tin, antimony, platinum, gold, mercury, lead and bismuth and a selenium compound selected from (a) selenourea, (b) an N-alkyl substituted selenourea of the formula:	
60		
65		



wherein  $R_1$ ,  $R_2$  and  $R_3$  are hydrogen atoms or alkyl groups, at least one of them being a hydrogen atom, and (c) a selenosemicarbazide of the formula:



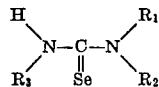
wherein one of  $R_{21}$  and  $R_{22}$  is a hydrogen atom or an alkyl, aralkyl or aryl group and the other of  $R_{21}$  and  $R_{22}$  is a hydrogen atom or an alkyl group,  $R_{23}$  is a hydrogen atom or an alkyl, aralkyl or aryl group, one of  $R_{24}$  and  $R_{25}$  is a hydrogen atom or an alkyl, aralkyl or aryl group and the other of  $R_{24}$  and  $R_{25}$  is a hydrogen atom or an alkyl group but at least one of  $R_{23}$ ,  $R_{24}$  or  $R_{25}$  being a hydrogen atom and there being not more than one group selected from aryl and aralkyl present in the compound, said oxidising agent being strong enough to bleach the silver but not strong enough to oxidise the silver halide solvent.

2. A process according to claim 1 wherein the mild oxidising agent is a ferric chelate complex.

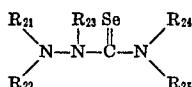
3. A process according to claim 2 wherein the ferric chelate complex is ferric ethylenediaminetetraacetic acid complex.

4. A process according to claim 1 wherein the bleach-fix accelerator is present in the bleach-fix bath.

5. A stable bleach-fix bath which comprises an aqueous solution of a mild oxidising agent, a thiosulphate and as a bleach-fix accelerator a complex consisting of a metal selected from iron, cobalt, nickel, copper, zinc, palladium, silver, cadmium, indium, tin, antimony, platinum, gold, mercury, lead and bismuth and a selenium compound selected from (a) selenourea, (b) an N-alkyl substituted



wherein  $R_1$ ,  $R_2$  and  $R_3$  are hydrogen atoms or alkyl groups, at least one of them being a hydrogen atom, and (c) a selenosemicarbazide of the formula:



wherein one of  $R_{21}$  and  $R_{22}$  is a hydrogen atom or an alkyl, aralkyl or aryl group and the other of  $R_{21}$  and  $R_{22}$  is a hydrogen atom or an alkyl group,  $R_{23}$  is a hydrogen atom or an alkyl, aralkyl or aryl group, one of  $R_{24}$  and  $R_{25}$  is a hydrogen atom or an alkyl, aralkyl or aryl group and the other of  $R_{24}$  and  $R_{25}$  is a hydrogen atom or an alkyl group but at least one of  $R_{23}$ ,  $R_{24}$  or  $R_{25}$  being a hydrogen atom and there being not more than one group selected from aryl and aralkyl present in the compound, said oxidising

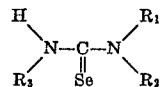
agent being strong enough to bleach the silver but not strong enough to oxidise the silver halide solvent.

6. A stable bleach-fix bath according to claim 5 wherein the mild oxidising agent is a ferric chelate complex.

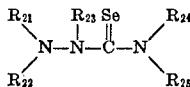
7. A stable bleach-fix bath according to claim 6 wherein the ferric chelate complex is ferric ethylenediaminetetraacetic acid complex.

8. A stable bleach-fix bath according to claim 5 wherein the concentration of bleach-fix accelerator is greater than 1 mg. per litre of bleach-fix bath.

9. A stop-fix bath which comprises an aqueous acid solution of a thiosulfate and a complex consisting of a metal selected from iron, cobalt, nickel, copper, zinc, palladium, silver, cadmium, indium, tin, antimony, platinum, gold, mercury, lead and bismuth and a selenium compound selected from (a) selenourea, (b) an N-alkyl substituted selenourea of the formula:



wherein  $R_1$ ,  $R_2$  and  $R_3$  are hydrogens atoms or alkyl groups, at least one of them being a hydrogen atom, and (c) a selenosemicarbazide of the formula:



wherein one of  $R_{21}$  and  $R_{22}$  is a hydrogen atom or an alkyl, aralkyl or aryl group and the other of  $R_{21}$  and  $R_{22}$  is a hydrogen atom or an alkyl group,  $R_{23}$  is a hydrogen atom or an alkyl, aralkyl or aryl group, one of  $R_{24}$  and  $R_{25}$  is a hydrogen atom or an alkyl or aryl group and the other of  $R_{24}$  and  $R_{25}$  is a hydrogen atom or an alkyl group but at least one of  $R_{23}$ ,  $R_{24}$  or  $R_{25}$  being a hydrogen atom and there being not more than one group selected from aryl and aralkyl present in the compound.

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