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3,748,136

PHOTOGRAPHIC SILVER BLEACHING SOLUTION
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38,508/70

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U.S. Cl. 96—60 R

17 Claims

ABSTRACT OF THE DISCLOSURE

A method of bleaching silver images in photographic elements by means of negatively charged oxidizing agents is described wherein said bleaching is accelerated by the use of onium compounds in the bleaching solution or in a solution used prior to the bleaching solution. The method makes possible to use as oxidizing agents the inexpensive and colourless persulphates which are otherwise too slow for silver bleaching.

The present invention relates to the bleaching of metallic silver by means of oxidizing agents in processes where photographic silver images are produced that should be bleached away more particularly to methods for accelerating said bleaching and to solutions used in said methods.

In the production of photographic images it is often necessary or desirable to bleach a silver image formed upon exposure and development by treatment with an oxidizing solution. Such oxidizing silver bleaching solutions are for instance used in so-called "toning" processes, in reversal processes, both colour and black-and-white, and in all other colour processes. A wide variety of oxidizing agents are used in said solutions such as water-soluble salts of the iron(III) ethylene diamine tetraacetic acid chelate, potassium dichromate, potassium hexacyanoferrate(III), potassium permanganate, cerium sulphate, etc. Owing to their favourable redox potential and the fact that they are colourless and inexpensive, persulfates, such as potassium, sodium, lithium and ammonium persulphate, would be most desirable silver bleaching agents. However, persulphates are not suitable for bleaching silver images because they are too slow silver bleaching agents.

It has now been found that silver bleaching by means of persulphates can be accelerated by the use of onium compounds as defined hereinafter. It was further found that said onium compounds do not only accelerate silver bleaching by means of persulphates but also silver bleaching by all kinds of negatively charged oxidizing agents such as dichromates for instance potassium, sodium and lithium dichromate and water-soluble salts of iron(III) ethylene diamine tetraacetic acid chelate.

Therefore, in accordance with the present invention there is provided a method of bleaching a metallic silver containing photographic element by treatment of the said metallic silver containing element with a solution comprising a negatively charged oxidizing agent in the presence of onium compounds comprising no anionic group in their molecule, which means that betaine salts are excluded, the said onium compound being present in the said solution or in a solution with which the silver image is treated before the treatment with the bleaching solution.

The invention further provides a photographic bleach solution which comprises a negatively charged oxidizing agent and such onium compound.

The onium compounds used in accordance with the present invention include:

(1) Basic mono-onium ternary trialkylsulphonium compounds, quaternary tetraalkyl phosphonium compounds, quaternary tetraalkyl ammonium compounds and

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quaternary ammonium compounds in which the quaternary N-atom is a member of a heterocyclic ring system, these onium compounds being characterised, unless the onium compound is a quaternary ammonium compound in which the quaternary N-atom is a member of a heterocyclic ring system having at least 5 conjugated double bonds, in that the sum of the carbon atoms of the groups linked to the onium atom is comprised between 8 and 24 and at least one of the said groups has at least 4 C-atoms and at most 14 C-atoms;

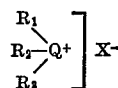
(2) Basic polyonium compounds;

(3) Oxido-reduction compounds the oxidized forms of which are onium compounds and which possess a polarographic half-wave potential measured at pH 3 in respect of the hydrogen electrode of at least 230 mv.

Among the mono-onium compounds suitable for being employed in practicing the present invention, those corresponding to the following general formulae are especially included:

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(I)



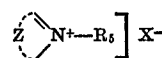
25 wherein:

Q⁺ stands for S⁺ or N⁺—R₄,

each of R₁, R₂, R₃ and R₄ stands for alkyl or two of them together represent the atoms necessary to complete a saturated heterocyclic ring such as a morpholine and piperidine ring, provided that at least one of the alkyl groups on the onium atom comprises at least 4 C-atoms and at most 14 C-atoms, and the total sum of the C-atoms in all R-groups on the onium atom is comprised between 8 and 24, and

X stands for an anion such as halide, p-toluene sulphonate, alkyl sulphate, perchlorate and persulphate;

40 (II)



wherein:

Z stands for the atoms necessary to complete a cyclammonium nucleus which may carry substituents and fused-on rings, for example pyridinium, 4-phenylpyridinium, α -picolinium, quinolinium, isoquinolinium, benzoquinolinium, imidazolinium, thiazolinium, benzo-thiazolinium, etc.,

R₅ stands for alkyl which, unless the cyclammonium nucleus completed by Z together with fused-on or substituent rings has at least 5 conjugated double bonds, comprises at least 8 C-atoms, and

X has the same significance as above.

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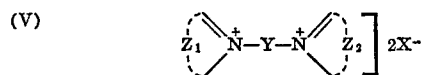
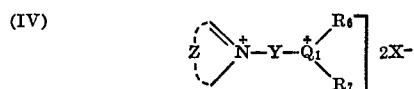
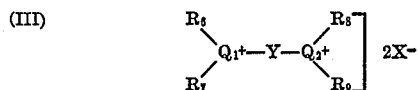
Representative examples of mono-onium compounds suitable for use according to the invention are:

- (1) 1-m-nitrobenzyl-quinolinium chloride
- (2) 1-dodecyl-pyridinium chloride
- (3) Dodecyl trimethylammonium p-toluene sulphonate
- (4) Dimethyl-nonyl sulphonium p-toluene sulphonate
- (5) N-methyl N-octyl morpholinium bromide.

Among the polyonium compounds suitable for being employed in accordance with the present invention those are included that contain an onium group selected from the group consisting of quaternary ammonium, quaternary phosphonium and ternary sulphonium, linked through its onium atom by at least one bivalent organic group, to the onium atom of another onium group selected from the group consisting of quaternary ammonium, quaternary phosphonium and ternary sulphonium groups. These poly-

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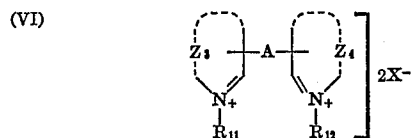
onium compounds can be represented by the following general formula:



wherein:

each of R_6 , R_7 , R_8 and R_9 stands for an alkyl group,
each of Q_1^+ and Q_2^+ , the same or different, stands for S^+ ,
 $N^+ - R_{10}$ or $P^+ - R_{10}$ wherein R_{10} stands for alkyl,
 Z and X have the same significances as above,
each of Z_1 and Z_2 , the same or different, have one of the significances given for Z , and
 Y stands for a bivalent organic group for example alkylene, alkylene interrupted by one or more oxygen or sulphur atoms, arylene and alkylene-arylene-alkylene.

Other suitable polyonium compounds are the diquaternary ammonium compounds represented by the following general formula:



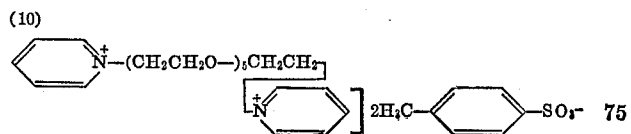
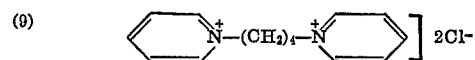
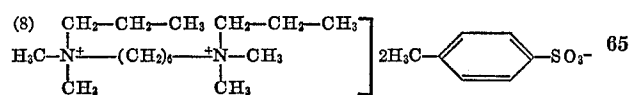
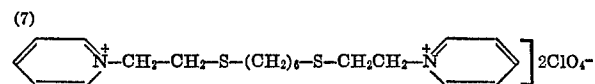
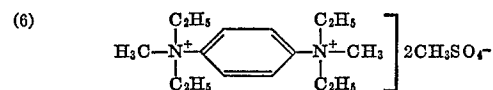
wherein:

X has the same significance as above,
each of Z_3 and Z_4 , the same or different, stands for the atoms necessary to complete a pyridinium, thiazolium or imidazolium nucleus optionally carrying fused-on aryl nuclei such as benzthiazolium, benzimidazolium and quinolinium and further substituents such as alkyl and aryl,

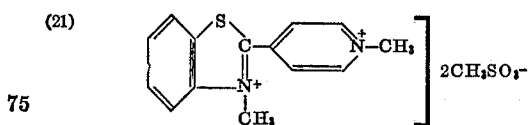
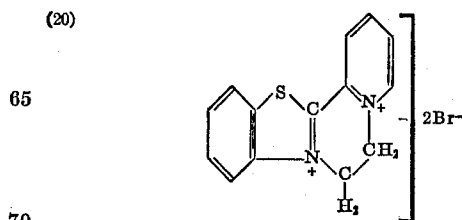
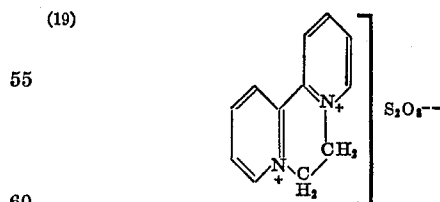
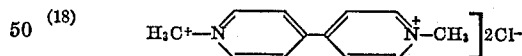
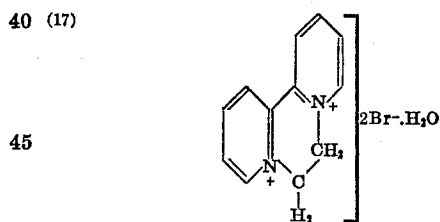
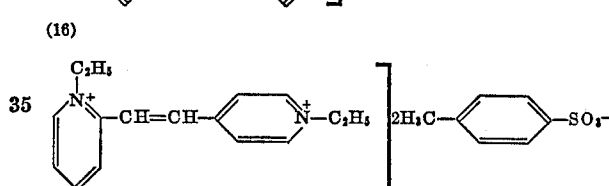
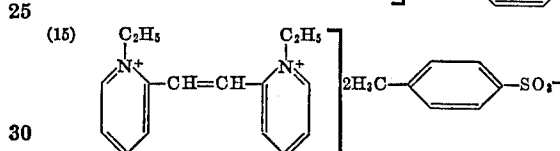
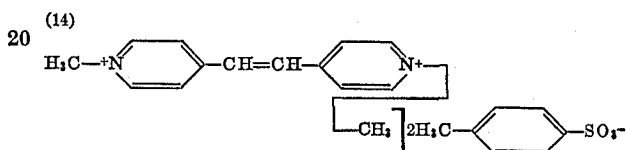
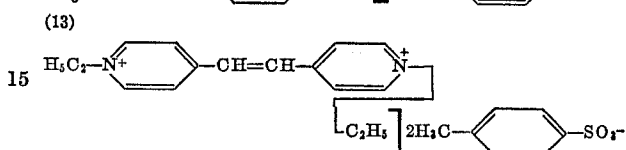
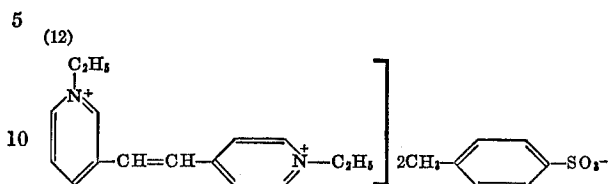
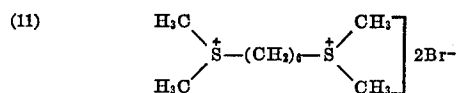
A stands for a chemical bond or the group $-\text{CH}=\text{CH}-$, and

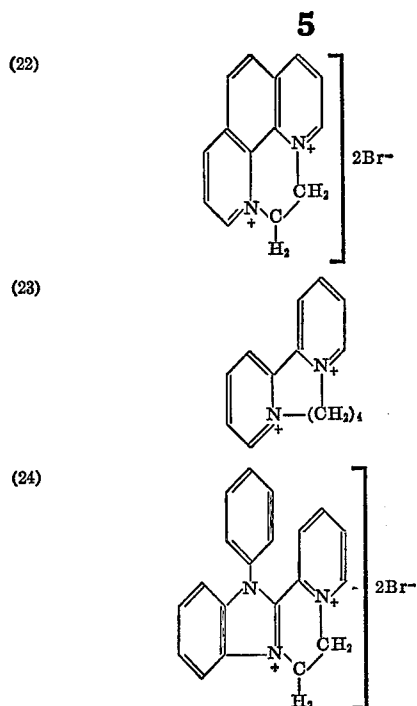
each of R_{11} and R_{12} stands for alkyl or, when A is a chemical bond linking the 2-position of Z_3 to the 2-position of Z_4 , together may be ethylene, trimethylene or tetramethylene.

Representative examples of polyonium compounds suitable for use according to the present invention are the compounds having the following formulae:



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Among the oxido-reduction compounds which in oxidized form are onium compounds and which possess a polarographic half-wave potential measured at pH 3 in respect of the hydrogen electrode of at least 230 mv., p-phenylene diamine derivatives such as N,N-dialkyl-p-phenylene diamines, N,N'-tetraalkyl - p - phenylene diamines and 1-alkyl-6-dialkylamino - 1,2,3,4 - tetrahydroquinolines can be most advantageously employed.

Other suitable oxido-reduction compounds are reversibly reducible dyestuffs such as Bindschedler's Green (C.I. 49,405), thiazine dyes for instance Methylene Blue (C.I. 52,015) and Lauth's Violet (C.I. 52,000), as well as oxazine and phenazine dyes. These oxido-reduction compounds may be used in acidic bleaching solutions in their reduced form, in their oxidized form as well as in their semiquinone form since by the acidic medium they are always in oxidized form.

In the method according to the present invention for accelerating the bleaching of metallic silver photographically formed in photographic silver halide elements by means of negatively charged oxidizing agents, it is essential that the onium compounds employed according to the invention are present in the bleaching solution the moment upon which the metallic silver is bleached. Therefore, the onium compounds are preferably incorporated into the bleaching solution. However, they may also be used in solutions with which the photographic element comprising photographically formed metallic silver is treated before bleaching e.g. a stop bath, a stop-fixing bath and a mere acidic solution of the said onium compounds.

The amount of onium compound used for accelerating the bleaching of metallic silver by means of negatively charged oxidizing agents may vary between very wide limits and depends on the particular onium compound used. The most suitable amount for the particular negatively charged oxidizing agent involved can be easily determined by some simple tests known to those skilled in the art. The ratio of negatively charged oxidizing agent to onium compound used according to the present invention is generally chosen so that the oxidizing agent strongly outweighs, even up to fifty times, the onium compound.

The bleaching solutions used in conjunction with the onium compounds according to the present invention may comprise in addition to the negatively charged oxidizing agents any of the common ingredients used in such solutions including silver halide solvents such as sodium thio-

sulphate as is used for instance in bleach-fixing solutions, sodium sulphite, alkali metal halides particularly alkali metal bromides, water softeners, thickening agents, hardeners, optical brightening agents, etc. Any of the materials used in bleach baths can be used to obtain the desired pH-value e.g. sulphuric acid, sulphamic acid, hydrochloric acid, phosphoric acid, acetic acid, boric acid, citric acid, sodium citrate, monosodium phosphate, sodium bisulphate, etc. The pH of the bleach solutions generally fall between a range of from 2 to 9, a pH between 3 and 6 being generally preferred.

The following examples illustrate the bleach-accelerating effect of the onium compounds used according to the invention.

EXAMPLE 1

Strips of positive fine grain film-type 5.61 available from Gevaert-Agfa N.V., Antwerp, Belgium, were overall exposed and developed in a conventional monomethyl-aminophenol/hydroquinone developer till a density of 2.40 was obtained whereupon the strips were fixed, washed and dried.

Each of these strips was treated with a bleaching solution comprising per litre 45 g. of potassium persulphate and 2.5 g. of potassium bromide as well as 2.66 millimole of an onium compound as listed in the table below.

The densities remaining after a treatment with the bleaching solution for 1 min., 3 min., 5 min. and 10 min. are listed in the table below.

TABLE

Onium compound added	Density after—			
	1 min.	3 min.	5 min.	10 min.
None.....	2.34	2.24	2.14	1.90
Compound:				
1.....	2.26	1.92	1.62	0.88
2.....	2.14	1.72	1.28	0.40
7.....	2.29	2.10	1.90	1.40
8.....	2.29	2.10	1.90	1.40
9.....	2.22	1.86	1.52	0.64
11.....	2.19	1.80	1.38	0.44

The above results clearly show that persulphates have only a very slow bleaching effect that can be accelerated by the use of the onium compounds.

EXAMPLE 2

This example is analogous to Example 1, with the difference that now the onium compounds listed in the table below were used.

The results shown in the table below prove the bleach-accelerating effect of the onium compounds.

TABLE

Onium compound added	Density after—			
	1 min.	3 min.	5 min.	10 min.
None.....	2.34	2.24	2.14	1.90
Compound:				
12.....	2.16	1.76	1.37	0.40
14.....	2.16	1.76	1.37	0.40
15.....	2.24	1.92	1.62	0.88
16.....	2.16	1.72	2.29	0.26
17.....	1.88	0.92	0.02	0.04
18.....	2.10	1.53	0.97	0.04
19.....	1.88	0.92	0.02	0.04
20.....	1.88	0.92	0.02	0.04
23.....	2.20	1.83	1.46	0.55

EXAMPLE 3

This example is analogous to Example 1, with the difference that now the oxido-reduction compounds listed in the table below were used instead of the onium compounds of Example 1.

The results listed below show the bleach-accelerating effect of the oxido-reduction compounds used.

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TABLE

Compound added	Density after—			
	1 min.	3 min.	5 min.	10 min.
None.....	2.34	2.24	2.14	1.90
Methylene Blue.....	2.24	1.94	1.66	0.95
Lauth's Violet.....	2.20	1.84	1.46	0.55
Bindschedler's Green.....	1.90	0.99	0.10	-----

EXAMPLE 4

This example is analogous to the preceding examples.

The results obtained by addition to the bleaching solution of the compounds listed in the table below are self-explanatory. The results also show that the p-phenylene diamines may be added to the acidic bleaching solution under no matter what form.

TABLE

Compound added	Density after—				
	1 min.	3 min.	5 min.	7 min.	10 min.
None.....	2.28	2.22	2.12	1.98	1.86
Compound 6.....	2.16	1.80	1.45	1.16	0.70
H_3C_2 N —  — $\text{NH}_2 \cdot \text{H}_2\text{SO}_4$ H_3C_2	2.24	1.96	1.72	1.48	1.12
H_3C_2 N —  — $\text{N}(\text{C}_2\text{H}_5)_2 \cdot 2\text{HCl}$ H_3C_2	2.08	1.42	0.78	10.4	-----
(reduced form)					
H_3C_2 N —  — $\text{N}^+(\text{C}_2\text{H}_5)_2$ H_3C_2	2.08	1.42	0.78	0.14	-----
(semiquinone form)					
H_3C_2 N^+ —  — $\text{N}^+(\text{C}_2\text{H}_5)_2$ H_3C_2	2.08	1.42	0.78	0.14	-----
(oxidized form)					

EXAMPLE 5

In this example varying amounts of compound 17 are added to the bleach solution of Example 1.

The results attained are listed in the table below.

TABLE

Compound 17 per litre bleach solution, g.	Density after—						
	1 min.	3 min.	4 min.	5 min.	8 min.	9 min.	10 min.
0.....	2.34	2.24	2.18	2.14	1.98	1.94	1.90
0.05.....	2.20	1.82	1.63	1.44	0.88	0.68	0.45
0.1.....	2.14	1.62	1.37	1.12	0.35	0.10	-----
0.2.....	2.10	1.60	1.20	0.96	0.06	-----	-----
0.5.....	1.94	1.04	0.60	0.10	-----	-----	-----
1.....	1.90	0.90	0.40	0.06	-----	-----	-----
2.....	1.80	0.72	0.20	0.06	-----	-----	-----

EXAMPLE 6

Strips of a film material as described in Example 1 were overall exposed and developed in a conventional monomethylaminophenol/hydroquinone developer till a density of 2.40 was obtained, whereupon the strips were fixed, washed and dried.

Each of these strips was treated with a bleaching solution of the following composition:

Sodium salt of the iron(III) chelate of ethylene diamine tetraacetic acid	18.7
Tetrasodium salt of ethylene diamine tetraacetic acid	6.25
Ammonium thiosulphate	55
Sodium sulphite	5
Ammonium thiocyanate	2.5
Water to make 1 litre.	

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to which per liter 2.66 millimole of an onium compound as listed in the table below was added.

The densities remaining after a treatment with the bleaching solution for 1 min., 3 min., 5 min., and 7 min. are listed in the table below.

TABLE

Compound added	Density after—			
	1 min.	3 min.	5 min.	7 min.
None.....	2.12	1.62	1.10	0.48
Compound:				
14.....	2.04	1.35	0.68	0.06
17.....	1.97	1.17	0.36	-----
18.....	1.97	1.17	0.36	-----

The above results show that the compounds of the invention also accelerate bleaching by means of iron(III) ethylene diamine tetraacetic acid.

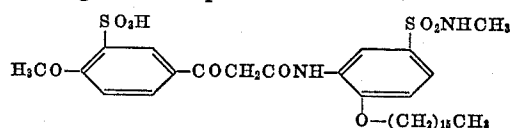
45 Yellow forming colour couplers that are present in the blue-sensitive silver halide emulsion layer of a photographic material give often rise to slow and difficult bleaching by dichromate-baths of the metallic silver

formed upon colour development. This manifests itself in high unwanted side-absorptions of the yellow dyestuff image formed.

The following examples illustrate the bleach accelerating effect of onium compounds when used together with bleaching solutions containing potassium dichromate as oxidizing agent.

EXAMPLE 7

A positive multilayer tricolour film-material comprising in the blue-sensitive silver halide emulsion layer the yellow-forming colour coupler of the formula:



was exposed through a blue filter and processed in the conventional way by the steps of treatment in a pre-bath, rinsing, colour development, fixing, rinsing, bleaching, rinsing, fixing and rinsing thus forming a yellow dye-image.

Bleaching took place for 2 min. in a bath of the following composition:

	G.
Potassium bromide	20
Potassium dichromate	5
Potassium alum (crystalline)	40
Water to make 1000 ml. (average pH: 3.1).	

The density of the image formed was then measured behind a blue, a green and a red filter and compared with the density of images formed under identical circumstances with the only difference that the bleaching bath contained one of the onium compounds listed in the table below.

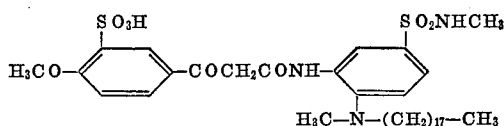
The results obtained are listed in the table.

TABLE

Onium compound added per liter of bleach bath	Density measured behind—		
	Blue filter	Green filter	Red filter
None.....	2.30	0.60	0.43
1 g. of compound 17.....	2.16	0.40	0.23
1 g. of compound 18.....	2.07	0.34	0.18

EXAMPLE 8

Example 7 was repeated with the difference that the material now contained the yellow-forming colour coupler of the formula:



and bleaching took place once for 2 min. and once for 4 min. The results attained are listed in the following table.

TABLE

Onium compound added per liter of bleach bath	Bleaching time, min.	Density measured behind		
		Blue filter	Green filter	Red filter
None.....	2	1.90	0.54	0.38
	4	1.78	0.33	0.16
1 g. of compound 17.....	2	1.70	0.30	0.14
	4	1.70	0.24	0.08
1 g. of compound 18.....	2	1.50	0.23	0.08
	4	1.46	0.22	0.07

I claim:

1. Method of bleaching a developed metallic silver containing photographic element with a solution containing a negatively charged oxidizing agent said solution containing an onium compound, or said developed element having been treated in a pre-bleaching bath, containing an onium compound, said onium compound comprising no anionic group in its molecule or a betaine structure and selected from the group consisting of:

(a) basic mono-onium trialkyl sulphonium compounds, quaternary tetraalkyl phosphonium compounds, quaternary tetraalkyl ammonium compounds and quaternary ammonium compounds in which the quaternary N-atom is a member of a heterocyclic ring system, wherein—unless the onium compound is a quaternary ammonium compound in which the quaternary N-atom is a member of a heterocyclic ring system having at least 5 conjugated double bonds—the sum of the carbon atoms of the groups linked to the onium atom is comprised between 8 and 24 and at least one of the said groups has at least 4 and at most 14 C-atoms;

(b) basic polyonium compounds, and

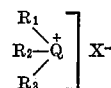
(c) oxido-reduction compounds the oxidized forms of which are onium compounds and which possess a polarographic half-wave potential measured at pH 3 in respect of the hydrogen electrode of at least 230 mv.

2. Method according to claim 1, wherein the said onium compound is present in the said solution of negatively charged oxidizing agent.

3. Method according to claim 1, wherein the said onium compound is present in a solution with which the metallic silver containing element is treated before the said treatment with a solution of a negatively charged oxidizing agent.

4. Method according to claim 1, wherein the said negatively charged oxidizing agent is a persulphate, a dichromate or a water-soluble salt of iron(III) ethylene diamine tetraacetic acid chelate.

5. Method according to claim 1, wherein the said onium compound is a mono-onium compound corresponding to the formula:



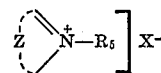
wherein:

Q⁺ stands for S⁺ or N⁺—R₄.

each of R₁, R₂, R₃ and R₄ stands for an alkyl group or two of them together represent the atoms necessary to complete a saturated heterocyclic ring, at least one of the alkyl groups on the onium atom comprising at least 4 and at most 14 C-atoms and the sum of the C-atoms in all R-groups on the onium atom being comprised between 8 and 24, and

X⁻ stands for an anion.

6. Method according to claim 1, wherein the said onium compound is a mono-onium compound corresponding to the formula:



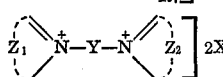
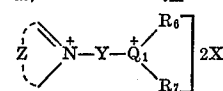
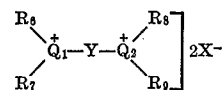
wherein:

Z stands for the atoms necessary to complete a cyclammonium group,

R₅ stands for an alkyl group which—unless the cyclammonium group completed by Z has at least 5 conjugated double bonds—comprises at least 8 C-atoms, and

X⁻ stands for an anion.

7. Method according to claim 1, wherein the said onium compound is a polyonium compound corresponding to one of the following general formulae:



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wherein:

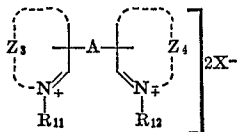
each of R_6 , R_7 , R_8 and R_9 stands for an alkyl group, each of Q_1^+ and Q_2^+ , the same or different, stands for S^+ , N^+-R_{10} , or P^+-R_{10} wherein R_{10} stands for an alkyl group,

each of Z , Z_1 and Z_2 stands for the atoms necessary to complete a cyclammonium group,

Y stands for a bivalent organic group, and

X^- stands for an anion.

8. Method according to claim 1, wherein the said onium compound is a polyonium compound corresponding to the formula:



wherein:

each of Z_3 and Z_4 , the same or different, stands for the atoms necessary to complete a pyridinium, thiazolium or imidazolium nucleus,

A stands for a chemical bond or the group $-\text{CH}=\text{CH}-$, each of R_{11} and R_{12} stands for an alkyl group or R_{11} together with R_{12} may be ethylene, trimethylene or tetramethylene when A is a chemical bond linking the 2-position of Z_3 to the 2-position of Z_4 , and X^- stands for an anion.

9. Method according to claim 1, wherein the said onium compound is the oxidized form of an oxido-reduction compound which possesses a polarographic half-wave potential measured at pH 3 in respect of the hydrogen electrode of at least 230 mv.

10. Method according to claim 9, wherein the said oxido-reduction compound is a N,N' -tetraalkyl-p-phenylene diamine or a 1-alkyl-6-dialkylamino-1,2,3,4-tetrahydroquinoline.

11. A photographic bleach solution comprising a negatively charged oxidizing agent and an onium compound selected from the group consisting of:

- (a) basic mono-onium trialkyl sulphonium compounds, quaternary tetraalkyl phosphonium compounds, quaternary tetraalkyl ammonium compounds and quaternary ammonium compounds in which the quaternary N-atom is a member of a heterocyclic ring system, wherein—unless the onium compound is a quaternary ammonium compound in which the quaternary N-atom is a member of a heterocyclic ring system having at least 5 conjugated double bonds—the sum of the carbon atoms of the groups linked to the onium atom is comprised between 8 and 24 and at least one of the said groups has at least 4 and at most 14 C-atoms;
- (b) basic polyonium compounds, and
- (c) oxido-reduction compounds the oxidized forms of which are onium compounds and which possess a polarographic half-wave potential measured at pH 3 in respect of the hydrogen electrode of at least 230 mv.

12. A photographic bleach solution to claim 11, wherein the said onium compound is a mono-onium compound corresponding to the formula:



wherein:

Q^+ stands for S^+ or N^+-R_4

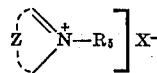
each of R , R_2 , R_3 and R_4 stands for an alkyl group or two of them together represent the atoms necessary to complete a saturated heterocyclic ring, at least one of the

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alkyl groups on the onium atom comprising at least 4 and at most 14 C-atoms and the sum of the C-atoms in all R-groups on the onium atom being comprised between 8 and 24, and

5 X^- stands for an anion.

13. A photographic bleach solution according to claim 11, wherein the said onium compound is a mono-onium compound corresponding to the formula:



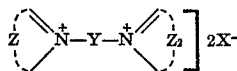
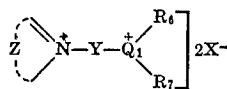
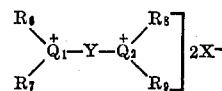
wherein:

15 Z stands for the atoms necessary to complete a cyclammonium group,

R_5 stands for an alkyl group which—unless the cyclammonium group completed by Z has at least 5 conjugated double bonds—comprises at least 8 C-atoms, and

20 X^- stands for an anion.

14. A photographic bleach solution according to claim 11, wherein the said onium compound is a polyonium compound corresponding to one of the following general formulae:



wherein:

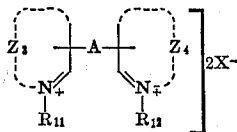
each of R_6 , R_7 , R_8 and R_9 stands for an alkyl group, each of Q_1^+ and Q_2^+ , the same or different, stands for S^+ , N^+-R_{10} , or P^+-R_{10} wherein R_{10} stands for an alkyl group,

45 each of Z , Z_1 and Z_2 stands for the atoms necessary to complete a cyclammonium group,

Y stands for a bivalent organic group, and

X^- stands for an anion.

15. A photographic bleach solution according to claim 11, wherein the said onium compound is a polyonium compound corresponding to the formula:



wherein:

each of Z_3 and Z_4 , the same or different, stands for the atoms necessary to complete a pyridinium, thiazolium or imidazolium nucleus,

A stands for a chemical bond or the group $-\text{CH}=\text{CH}-$, each of R_{11} and R_{12} stands for an alkyl group or R_{11} together with R_{12} may be ethylene, trimethylene, tetramethylene when A is a chemical bond linking the 2-position of Z_3 to the 2-position of Z_4 , and X^- stands for an anion.

16. A photographic bleach solution according to claim 11, wherein the said onium compound is the oxidized form of an oxido-reduction compound which possesses a polarographic half-wave potential measured at pH 3 in respect of the hydrogen electrode of at least 230 mv.

17. A photographic bleach solution according to claim 16, wherein the said oxido-reduction compound is a N,N' -

tetraalkyl-p-phenylene diamine or a 1-alkyl-6-dialkyl-amino-1,2,3,4-tetrahydroquinoline.

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M. F. KELLEY, Assistant Examiner

U.S. Cl. X.R.

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