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(54) **Silver halide photographic emulsions**

(57) A process for chemical sensitization of silver halide photographic emulsions comprises adding as sensitizing agents a 40 - 260 μM/M amount (calculated for the silver halide) of a cyclooctadecane containing nitrogen and 5 oxygen atoms, or 2 nitrogen and 4 oxygen atoms, or 3 nitrogen and 3 oxygen atoms, for 4 nitrogen and 2 oxygen atoms as well as 12 carbon atoms and/or their complexes formed with gold and/or palladium and optionally 40 - 260 μM/M (calculated for the silver halide) or gold(I) or gold(III) sulfide to the sulfur-sensitized emulsion, and employing the cyclooctadecane in relation to the noble metal salt in a molar ratio of 0.5:1 – 5:1 for the complex formation.

This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1990.

SILVER HALIDE PHOTOGRAPHIC EMULSIONS

The invention relates to a process for the chemical sensitization of silver halide photographic emulsions by cyclic polyethers and/or their noble metal complexes and to such sensitized emulsions.

For the chemical sensitization of silver halide photographic emulsions, combinations of labile sulfur and gold compounds are most widely used. The sulfur compounds develop on the crystal surfaces silver sulfide centres, from which mainly a gold sulfide or (gold, silver) sulfide arises under effect of the gold compound. Thus, sensitivity is increased, fog is diminished, reciprocity failure occurring under high intensity illumination is improved and solarization is suppressed. Useful labile sulfur compounds include inter alia the thiosulfate, and gold(I) and gold(III) complexes may be employed as the gold compounds [see E. Moisar: Phot. Sci. Eng. 25:45 (1981)].

Considering that gold(III) reacts with gelatin (which, according to most recent investigations, is due to methionine being present in the polypeptide chain), gold(I) complexes are preferred for gold sensitization. The gold(I) isothiocyanate complex formed by the interaction of SCN^- and $AuCl_4^-$ ions, which is the result of an autoreduction in the presence of a high thiocyanate excess, has been used for a long time. Nevertheless, unfavourable properties of the emulsion may also be developed by its use, e.g.: a) the efficiency of sensitization is reduced by chelate formation of gold(I) with gelatin; b) effects of reducing substances on the gelatin metallic gold arise which induce fogging; c) due to the thiocyanate being present in excess, a crystal increase occurs also during the chemical ripening whereby the covering ability is reduced and the image tone turns into grey in emulsions giving a brown tone.

To eliminate these defects other gold compounds have been suggested, such as e.g. dithiosulfate-mono-aurate(I) which is better adsorbed on silver halide crystals and has a stronger sensitizing effect but makes the sensitivity distribution strongly heterogeneous and, therefore, gives the possibility of preparing emulsions only with smooth gradation; in addition, depending on the sulfur sensitizer, it may also induce fogging.

Various water-soluble and water-insoluble gold mercaptides, quaternary gold salts, gold sulfide, gold selenide and the like (see United States Patents Nos. 2,597,915, 2,642,361, 3,408,197 and 3,503,749) are also suitable for gold sensitization but they are not so effective as gold thiocyanate or gold thiosulfate.

The supersensitization of sulfur- and gold-sensitized emulsions by palladium(II) salts has been described in the early 50's (see United States Patent No. 2,598,079). Nevertheless, the sensitivity was diminished by using $[PdCl_4]^{2-}$ together with gold thiosulfate; by using gold thiocyanate alone, the sensitivity was increased, however, the fog was also strengthened [see L. De Brabandere and P. Faelens: Phot. Sci. Eng. 25:63 (1981)]. The sensitivity of the emulsion treated with gold alone was significantly increased by the palladium(II) complexes of some N-alkylated polyamines but its value did not exceed those obtained by sulfur- plus gold-sensitization while the fogging was not changed. When a suitable palladium(II) complex was added to a sulfur- plus gold-sensitized emulsion, the maximum sensitivity was not further increased, and while the duration of ripening required for reaching the highest sensitivity was shortened the fogging value remained unchanged [see J. Hartung et al.: J. Inf. Rec. Mater. 14:417

(1986)]. In addition to these effects, part of the Pd^{2+} introduced to the emulsion may also be lost for the sensitization due to the interaction of palladium(II) with gelatin [see K. Tanaka: J. Phot. Sci. 21:134 (1973)], depending on the stability of the palladium(II) complex used.

Thus, an objective of the present invention is to provide a sensitization process, by means of which sensitivity may be further improved, a narrower sensitivity distribution of the crystals may be achieved and other unfavourable effects may be eliminated.

The invention is based on the recognition that gold or palladium ions form inclusion complexes with certain macrocyclic compounds.

Thus viewed from one aspect the invention provides a silver halide photographic emulsion comprising a sensitizing agent comprising a macrocyclic polyether and/or a gold and/or palladium complex thereof.

Viewed from a further aspect the invention also provides a process for the chemical sensitization of silver halide photographic emulsions which comprises incorporating in a said emulsion as an additional sensitizing agent a macrocyclic polyether and/or a gold and/or palladium complex thereof.

Viewed from a yet further aspect the invention also provides a photographic substrate coated with an emulsion according to the invention.

The macrocyclic polyethers used according to the invention are preferably azaoxacyclododecanes, especially those containing one ring nitrogen and five ring oxygens, two ring nitrogens and four ring oxygens, three ring nitrogens and there ring oxygens or four ring nitrogens and two ring oxygens (together with twelve ring carbons).

The polyether or the complex thereof is preferably added at 40-260 µM/M relative to the silver halide and optionally a gold(I) or gold(III) sulfide is also added to the sulfur-sensitized emulsion, again preferably at 40-260 µM/M relative to the silver halide.

Where a complex of the polyether is used it is preferably formed employing the polyether relative to the noble metal salt in a molar ratio of 0.5:1 to 5:1.

The 18-membered crown ethers containing oxygen and nitrogen, which are macrocyclic compounds, are capable not only of forming gold or palladium complexes but also of reducing noble metal ions in the course of complex formation.

When used either separately or in combination, the complexes formed from the above-mentioned gold or palladium salts with the macrocyclic compounds are able to increase the sensitivity of sulfur-sensitized crystals and a synergistic effect appears on their simultaneous use.

It is considered that the reducing effect of the crown ethers also contributes to the increase in the sensitivity.

An additional sensitivity increase results from the combination of the use of above-mentioned complexes of gold and palladium salts with the use of gold sulfide.

Crown ethers are cyclic polyethers which are able to incorporate cations in their central cavities. The salt complexes are formed under the ion-dipole interaction of the cation with the heteroatoms (e.g. oxygen or nitrogen) present in the polyether ring. The most important conditions required for the formation and factors influencing the stability of the complexes are:

1. relative dimensions of the ion and the central cavity of

the polyether ring;

2. the number and disposition of the heteroatoms in the cyclic polyether;

3. the electrical charge of the ions and the like.

The formation of the complex is indicated by the facts that the solubility of both the polyether and salt are altered in various solvents; the UV spectrum of the polyether shows a characteristic change; and the conductivity of the salt solution is also altered [see J. Pederson: J. Am. Chem. Soc. 89:7017 (1967)].

Although many hundreds of complexes have been described since the preparation of the first crown ethers [see R. M. Izatt et al.: Chem. Rev. 85:271 (1985); I. Bernal: Stereochemical and Stereophysical Behaviour of Macrocycles, Elsevier, Amsterdam, pages 151, 161, 173-177 and 191-204 (1987)], no gold(I) compound has been reported and complexes of palladium formed only with 15- and 18-membered crown ethers containing sulfur, nitrogen and oxygen have been described. The former circumstance is related to the fact that gold(I) is more liable to form stable linear complexes. Notwithstanding this, our conductometric examinations have shown that complex formation occurs on interaction of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane and $HAuCl_4$, a finding which is supported by the strong decrease in the conductivity (Table 1).

Table 1

Concentration of $HAuCl_4$ M/litre	Concentration of crown ether (CE) M/litre	$\frac{[CE]}{[Au]}$	Ω μS
10^{-3}	-	-	420
10^{-3}	$0.5.10^{-3}$	0.5	245
10^{-3}	$1.0.10^{-3}$	1	175
10^{-3}	$1.5.10^{-3}$	1.5	105
10^{-3}	$3.0.10^{-3}$	3	98
10^{-3}	$5.0.10^{-3}$	5	7

Thus viewed from a further aspect the invention also provides complexes of an azaoxacyclododecane macrocyclic polyether (especially thia-free azapolyoxa- and polyazapolyoxa- cyclododecanes) with gold (especially gold(I)) and palladium.

In our opinion, the role of stability of complexes formed from noble metal salts with cyclic polyethers in the sensitization can be defined in such a way that the complex has to be sufficiently stable to prevent the interaction of the metal ions with gelatin and, on the other hand, it should be able to adsorb on the crystals and then to release the metal ion for the sensitization.

The reduction occurring in the course of complex formation, e.g. the conversion of Au^{3+} to Au^{+} was demonstrated by oxidation-reduction potential measurements carried out with a Pt/calomel electrode pair (Table 2).

Table 2

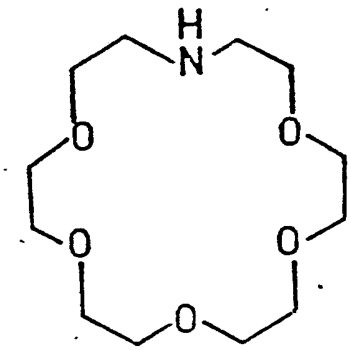
Concentration of $HAuCl_4$ M/litre	Concentration of Compound II M/litre	Oxidation-reduction potential at 25°C mV
10^{-4}	-	+ 393
10^{-4}	10^{-4}	+ 210
10^{-4}	2.10^{-4}	+ 142
10^{-4}	3.10^{-4}	- 38

In the process according to the invention an amount of 40 - 260 μM/M of a cyclic polyether containing 1 nitrogen and 5 oxygen atoms, or 2 nitrogen and 4 oxygen atoms, or 3 nitrogen and 3 oxygen atoms, or 4 nitrogen and 2 oxygen atoms as well as 12 carbon atoms and/or their complexes formed with gold and/or palladium are used for an additional sensitization of sulfur-sensitized silver halide photographic emulsions while employing the cyclic polyether and the noble metal salt in an 0.5:1 - 5:1 molar ratio.

According to an other embodiment of the process of the invention a 40 - 260 μM/M amount of gold(I) sulfide or gold(III) sulfide are also used in addition to the cyclic polyether and/or its complex(es) formed with gold and/or palladium for the sensitization.

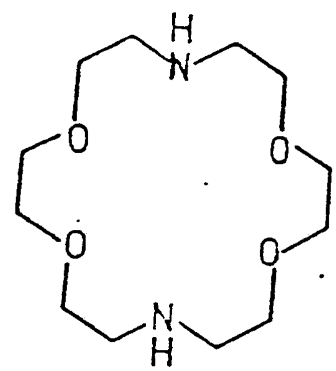
Polyethers, being useful in the process of the invention, include e.g.

1-aza-4,7,10,13,16-pentaoxacyclooctadecane of formula (I)



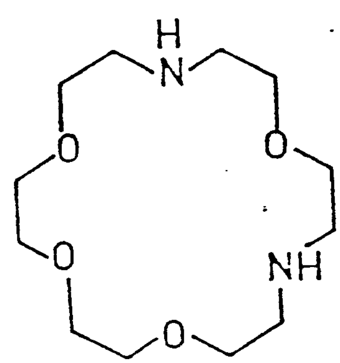
(I)

1,10-diaza-4,7,13,16-tetraoxacyclooctadecane of formula (II),



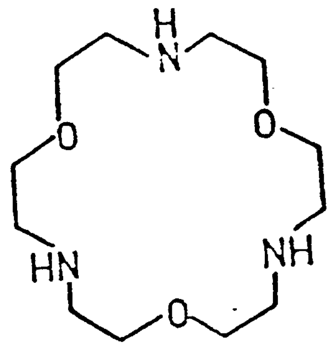
(II)

1,7-diaza-3,10,13,16-tetraoxacyclooctadecane of formula (III),



(III)

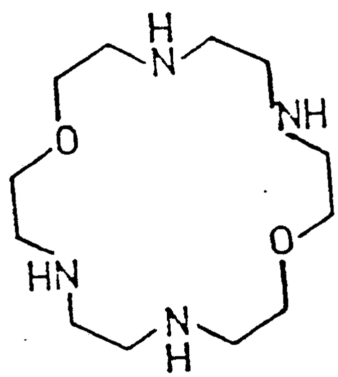
1,7,13-triaza-4,10,16-trioxacyclooctadecane of formula (IV)



(IV)

and

7,16-dioxa-1,4,10,13-tetraazacyclooctadecane of formula (V)



(V)

For carrying out the invention, the inclusion complex may be prepared by introducing the required amount of an aqueous solution containing the noble metal salt to a solution of the cyclic polyether in an organic solvent, e.g. methanol or ethanol. Useful noble metal ions or compounds are e.g. $[AuCl_4]^{-1}$, $[Au(SCN)_2]^-$, $[PdCl_6]^{2-}$, $[PdCl_4]^{2-}$, $PdCl_2$, $[Pd(SCN)_4]^{2-}$ and the like.

The advantages of the process according to the invention may be summarized as follows:

1) The efficiency of the sensitization can significantly be increased in comparison to the known sensitizing processes using noble metals.

2) The tendency to fogging is diminished.

3!) The sensitivity can be strengthened without any decrease in the gradation.

The present invention is further illustrated by the following non-limiting Examples.

Example 1

500g of an Ag(Br,Cl) emulsion (with an inert gelatin content of 8%; crystal size of 170 nm, variation coefficient of 20% and chloride excess of 30 mole%) are subjected to a chemical ripening at 55°C. In the 0. minute of the ripening 85 µM/M of the sulfur sensitizer, e.g. the complex of phenylrhodanine with carboxymethyl-ß-cyclodextrin polymer (see M. Szücs et al., United Kingdom Patent No. 2,160,993) are added to the emulsion, then other cehmical sensitizers are added in the 15th minute and the chemical ripening is continued at the same temperature for an additional 85 minutes.

After cooling down, 2 ml of a 0.05 % solution of 3,3'-diethyl-1'-phenylbenzoxazylidene-ethylidene-2'-thiohydantoine, 2 ml of 50 % glycerol solution, 5 ml of 4 % saponin solution, 5 ml of 8 % 2-hydroxy-4,6-dichloro-s-triazine solution and 1 ml of an 1 % phenylmercaptotetrazole solution are added at 40 °C to 100 g of the above emulsion. Thereafter, the emulsion is applied on a baryta-coated paper base with a surface silver content of 1.15 ± 0.05 g/m^2.

For plotting the characteristic curve, the photographic material is illuminated through a photographic modulator by a lamp with a colour temperature of 2850 °K and then developed at 18 °C for 2 minutes in a developer containing 1 g of methol, 4 g of hydroquinone, 20 g of anhydrous sodium sulfite, 10 g of anhydrous sodium carbonate and 1 g of potassium bromide in 1 litre of water.

The results are shown in Table 3. It is obvious from this table that gold complexes of cyclic polyethers used in the process according to the invention exert a higher sensitizing effect with lower fogging values than other gold compounds do and, in addition, they give a higher gradation.

It can also be stated that cyclic polyethers, even when used alone and mainly in higher doses, possess a significant sensitizing effect while resulting a lower gradation and eventually a somewhat higher fogging value than their gold complexes do.

TABLE 3

Other sensitizers Name	Dose µM/M	S_{rel}	$\bar{G}$	D_o 18°C, 2 min	D_o 30°C, 5 min
None	-	100	2.04	0.05	0.26
$[Au(SCN)_2]^-$	85	165	1.90	0.09	0.37
$[Au(S_2O_3)]^-$	85	178	1.35	0.08	0.29
Au_2S_3	85	145	1.80	0.08	0.30
Compound (II)	150	120	1.68	0.06	0.21
	200	160	1.75	0.07	0.25
	255	200	1.80	0.08	0.27
Gold complex of	42.5	206	2.01	0.06	0.16
compound (II)	85	239	2.11	0.06	0.22
[(II)]/[Au] = 3	127.5	256	2.10	0.06	0.30
	170	191	1.96	0.08	0.32
Gold complex of					
compound (II)					
[(II)]/[Au] = 0.5	85	169	1.93	0.06	0.20
1.5	85	188	2.06	0.06	0.20
3	85	239	2.11	0.06	0.22
5	85	200	2.05	0.09	0.22
Compound (IV)	150	132	1.52	0.08	0.22
	200	196	1.60	0.08	0.28
	255	216	1.62	0.08	0.30
Gold complex of	42.5	200	1.90	0.07	0.24
compound (IV)	85	219	1.98	0.08	0.27
[(IV)]/[Au] = 3	127.5	226	2.07	0.08	0.30
Gold complex of	42.5	190	1.50	0.09	0.28
compound (V)	85	211	1.58	0.09	0.32
[(V)]/[Au] = 1.5	127.5	215	1.58	0.09	0.36

Example 2

The process described in Example I is followed, except that gold sulfide in 10th minute of the ripening and in 25th minute of ripening, the gold complex of Compound (II) ([II] / [Au] = 3) is introduced to the emulsion. The results are summarized in Table 4.

Table 4

Gold sulfide Comps-sition	Dose 5 min μM/M	Addition of complex μM/M	S_{rel}	$\overline{G}$	D_o 18°C, 2 min	D_o 30°C, 5 min
Au_2S_3	0	0	100	2.04	0.05	0.22
	85	85	270	2.10	0.05	0.28
	170	85	318	2.15	0.06	0.32
	255	85	330	2.18	0.06	0.34
Au_2S	127.5	0	180	2.32	0.06	0.32
	127.5	42.5	232	2.38	0.07	0.36
	127.5	85	279	2.40	0.07	0.38
	127.5	127.5	302	2.35	0.09	0.39

It is clearly shown by the results that in comparison to the emulsion containing a sulfur sensitizer alone, the sensitivity can further be increased by using a combination of gold complex of the cyclic polyether with gold sulfide.

Example 3

500 g of an Ag(Br,Cl) emulsion (with an inert gelatin content of 9.1 %, iodide content of 0.9 mole%, pBr = 3.0, crystal size of 425 nm, variation coefficient of 25%) are

subject to a chemical ripening at 63°C. In the 0. minute of the ripening 50 μM/M of the sulfur sensitizer (see Example 1), in the 15th minute Au_2S_3, in the 20. minute gold complex are added and the chemical ripening is continued at the same temperature for additional 100 minutes. After cooling down, 1.5 ml of an 50% glycerol solution, 5.8 ml of an 8% 2-hydroxy-4,6-dichloro-s-triazine solution, 5 ml of 4% saponin solution and 2.5 ml of 1% 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindole solution are added at 40°C to 100 g of the above solution. Thereafter, the emulsion is applied onto a cellulose triacetate base with a surface silver content of 3.0±0.15 g/m^2. The sensitometric characteristics are determined according to the ANSI PH 2.5-1972 standard (with a developing time of 7 minutes). The results are summarised in Table 5.

Table 5

Dose of Au_2S_3 μM/M	Gold complex or other sensitizers Name	Dose μM/M	S_{rel}	$\bar{G}$	D_0
0	-	-	100	0.60	0.11
0	Compound (I)	150	135	0.58	0.10
		200	150	0.59	0.12
		250	162	0.61	0.14
0	Compound (III)	150	151	0.63	0.15
25	$[Au(SCN)_2]^-$	50	150	0.62	0.08
25	$[Au(S_2O_3)]^-$	50	159	0.58	0.12
25	Gold complex of	25	198	0.63	0.10
	compound (I)	50	212	0.62	0.11

Table 5

(contd.)

Dose of Au_2S_3 μM/M	Gold complex or other sensitizers Name	Dose μM/M	S_{rel}	$\bar{G}$	D_0
	[(I)]/[Au] = 1.5	100	230	0.64	0.13
50	Gold complex of	25	180	0.56	0.09
	Compound (III)	50	192	0.58	0.11
	[(III)]/[Au] = 3	100	201	0.61	0.12

It is shown by the data that the combinations of gold complexes of cyclic polyethers with gold sulfide ensure a higher sensitivity increase than the usual gold complexes.

Example 4

The process described in Example 1 is followed, except that the sulfur sensitizer is added in an amount of 100 μM/M and in the 5th minute after its addition additive <u>A</u>, in the 10th minute additive <u>B</u>, in the 15th minute additive <u>C</u> are added to the emulsion. The results obtained are illustrated in Table 6.

Table 6

A	μM/M	B	μM/M	C	μM/M	S_{rel}	$\bar{\bar{G}}$	D_o 18°C,2min	30°C,5min
0		0		0		100	2.30	0.04	0.20
C1	127.5	C2	85	-		221	2.18	0.06	0.24
	127.5		170	-		280	2.21	0.06	0.25
	127.5		255	-		312	2.16	0.06	0.24
C2	85	-		-		169	2.39	0.07	0.20
	170	-		-		173	2.40	0.07	0.21
	255	-		-		178	2.35	0.08	0.22
C3	127.5	C2	127.5	-		230	2.26	0.06	0.24
	170		127.5	-		272	2.19	0.08	0.25
	255		127.5			306	2.06	0.08	0.28
C1	85	C3	85	C2	85	325	2.26	0.08	0.32
	85		85		170	356	2.21	0.09	0.34
	85		85		255	365	2.28	0.08	0.33

Notes to Table 6:

C1: Gold complex of Compound (II), [(II)]/[Au] = 1.5

C2: the complex of Compound (II) with $(NH_4)_2PdCl_4$,
[(II)]/[Pd] = 1.5

C3: Au_2S

It is obvious from the above results that the palladium complex of Compound (II) in sulfur-sensitized emulsion ensures the same grade of sensitivity increase as the gold complex does and, on the other hand, the combination of palladium(II) and gold(I) complexes permits a higher sensitivity increase than these do separately in the same doses. It is also obvious that the combination of the palladium complex with gold sulfide also results in a significant sensitivity increase.

Claims:

1. A silver halide photographic emulsion comprising a sensitizing agent comprising a macrocyclic polyether and/or a gold and/or palladium complex thereof.

2. An emulsion as claimed in claim 1 wherein said polyether comprises a cyclooctadecane macrocycle having six ring oxygen and nitrogen heteroatoms, at least one of which is nitrogen and at least two of which are oxygen.

3. An emulsion as claimed in either of claims 1 and 2 wherein said polyether or complex thereof is present at 40-260 μM/M relative to the silver halide.

4. An emulsion as claimed in any one of claims 1 to 3 further comprising a gold(I) or gold(III) sulfide.

5. A composition as claimed in claim 4 wherein said gold sulfide is present at 40-260 μM/M relative to the silver halide.

6. An emulsion as claimed in any one of claims 1 to 5 containing a said complex formed by reaction of the polyether and the gold or palladium in a molar ratio of 0.5:1 - 5:1.

7. An emulsion as claimed in any one of claims 1 to 6 wherein said polyether is a monoazapentaoxacyclododecane.

8. An emulsion as claimed in any one of claims 1 to 6 wherein said polyether is 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane.

9. An emulsion as claimed in any one of claims 1 to 6 wherein said polyether is 1,7-diaza-3,10,13,16-tetraoxacyclooctadecane.

10. An emulsion as claimed in any one of claims 1 to 6 wherein said polyether is 1,7,13-triaza-4,10,16-trioxacyclooctadecane.

11. An emulsion as claimed in any one of claims 1 to 6 wherein said polyether is 7,16-dioxa-1,4,10,13-tetraazacyclooctadecane.

12. Photographic substrates coated with an emulsion as claimed in any one of claims 1 to 11.

13. A process for the chemical sensitization of silver halide photographic emulsions which comprises incorporating in a said emulsion as an additional sensitizing agent a macrocyclic polyether and/or a gold and/or palladium complex thereof.

14. A process as claimed in claim 13 which comprises adding as an additional sensitizing agent 40 - 260 µM/M relative to the silver halide of a said macrocyclic polyether containing 1 ring nitrogen and 5 ring oxygen atoms, or 2 ring nitrogen and 4 ring oxygen atoms, or 3 ring nitrogen and 3 ring oxygen atoms, or 4 ring nitrogen and 2 ring oxygen atoms as well as 12 ring carbon atoms and/or a gold and/or palladium complex thereof and optionally 40 -260 µM/M relative to the silver halide of a gold(I) or gold(III) sulfide to a sulfur-sensitized emulsion, the cyclic polyether in relation to the noble metal salt being employed in a molar ratio of 0.5:1 - 5:1 for the complex formation.

15. A process as claimed in claim 13 or 14, which comprises using a monoazapentaoxacyclooctadecane as a cyclic polyether.

16. A process as claimed in claim 13 or 14, which comprises using 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane as a cyclic polyether.

17. A process as claimed in claim 13 or 14, which comprises using 1,7-diaza-3,10,13,16-tetraoxacyclooctadecane as a cyclic polyether.

18. A process as claimed in claim 13 or 14, which comprises using 1,7,13-triaza-4,10,16-trioxacyclooctadecane as a cyclic polyether.

19. A process as claimed in claim 13 or 14, which comprises using 7,16-dioxa-1,4,10,13-tetraazacyclooctadecane as a cyclic polyether.

20. Complexes of an azaoxacyclododecane macrocyclic polyether with gold and/or palladium.

21. Macrocyclic polyether containing photographic emulsions substantially as herein disclosed.

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