PATENT SPECIFICATION (11) 1 574 787

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(21) Application No. 28793/77 (22) Filed 8 Jul. 1977

(31) Convention Application No. 703405 (32) Filed 8 Jul. 1976 in

(33) United States of America (US)

(44) Complete Specification Published 10 Sep. 1980

(51) INT. CL.[3] G03C 5/42
B41M 5/26
C07C 151/00 154/00 157/00
C07F 9/30
G03C 1/72

(52) Index at Acceptance
G2C B6Y CXB H6A7 H6C4
C2C 200 20Y 222 227 22Y 292 29Y 30Y
364 36Y 372 373 374 37Y 380 461
465 551 634 68X 755 75X 76X 771
78Y AA QQ SM
C2P 3D 5B 7

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(54) PROCESS OF MAKING TELLURIUM IMAGES

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a process of making tellurium images.

Many photographic imaging processes are known, including the widely used silver halide processes and "non-conventional" processes such as diazo processes, photopolymerization processes and various direct printout and photochromic processes which use sensitive materials which are mostly slower than silver halide materials. A process providing a good photographic speed generally contains an amplification step, imagewise exposure being required to produce only a minute, and normally invisible, amount of a catalytic substance and the much greater amount of material needed to form a visible image being provided by using the catalytic substance to catalyze a chemical reaction, usually the reduction of a metal compound to the free metal. In silver halide processes for example, exposure of silver halide grains to light results in the formation of silver nuclei (latent image specks) which then catalyze the reduction of more silver halide by a reducing agent.

According to the present invention there is provided a method of making a visible image which comprises forming an imagewise distribution of nuclei of tellurium, palladium, silver, copper or a mixture of two or more of these, and employing said distribution to catalyze the decomposition of a coordination complex of tellurium (II) in which at least one ligand contains a sulphur atom by which it is coordinated to the tellurium atom.

The method of the invention can be implemented in a variety of ways. The first step, formation of an imagewise distribution of nuclei of the specified element (or mixture of elements) can, for instance, be carried out by exposing one or more radiation-sensitive compounds, or by exposing one or more reducible compounds (which need not be radiation-sensitive) in the presence of a photoreductant, or by vapour deposition of the desired element on a substrate. The second step, employing the imagewise distribution of nuclei to catalyze decomposition of the specified tellurium (II) complex can, for instance, be carried out by incorporating the complex in the layer in which the nuclei are formed, or a layer adjacent thereto and, if necessary, heating or by treating the layer containing the nuclei with a solution of the complex.

In a preferred embodiment of the present invention, a photosensitive tellurium (II) complex is coated on a support. Upon exposure, the complex decomposes to give elementary tellurium which functions as a catalyst for the further decomposition of the

tellurium (II) complex, when the conditions are appropriate, for example when the material is heated or treated with a solvent.

Where the tellurium (II) complex is to be the source of catalytic nuclei, a photoreductant may be incorporated in the material to facilitate the formation of the tellurium catalytic nuclei. If this is done, the tellurium complex need not be photosensitive.

As used herein, the term "photoreductant" means a material capable of molecular photolysis or photoinduced rearrangement of generating a reducing agent capable of reducing the tellurium (II) complex.

Useful classes of photoreductants include quinones, disulphides, diazoanthrones, diazophenanthrones, carbazides, diazosulphonates, diazonium salts, aromatic azides, benzimidazoles and aziridines as described in Item No. 12617 of *Research Disclosure*, October 1974, pp. 13-14, and as exemplified in Table I, pp. 14-17 thereof.

Various light-sensitive inorganic compounds are useful as photoreductants including ferric salts, vanadic, tungstic, and molybdenum compounds and uranium salts as described, for example, in British Patent 670,883. Particular compounds include ferric ammonium citrate, sodium metavanadate, sodium molybdate-oxalate and sodium tungstate oxalate.

Conventional inorganic photoconductors such as titanium dioxide and zinc oxide may also be employed to photoreduce the Te(II) complexes of this invention. These inorganic compounds are described in *Jour. Electrochem. Soc.*, *121*, 1160 (1974) and *122*, 1103 (1975) and in U.S. Patents 3,652,276 and 3,862,352.

Certain tellurium (II) complexes of the present invention undergo spontaneous decomposition after being exposed to heat. Sensitive materials which incorporate these complexes yield an image without the need for further treatment, i.e., they "print out".

In another method of the invention, the tellurium complex may be coated in a material together with a separate photosensitive compound such as a silver halide, a palladium complex or a copper complex. Exposure of the photosensitive material then produces nuclei which act as a catalyst for the thermal decomposition of the tellurium complex.

In another method of the invention a solution of the tellurium complex is used as a physical developer solution, developing the imagewise distribution of nuclei to a visible image.

The complexes used for the present invention are complexes of tellurium (II), which has a coordination number of four, and are characterized in that at least one of the coordinating ligands coordinates to the tellurium through a sulphur atom. Any number of the tellurium (II) coordination positions may be occupied by the sulphur atom of a suitable sulphur-containing ligand. The tellurium (II) may therefore be coordinated with a monodentate, bidentate or tridentate sulphur-containing ligand or with a combination of such ligands. The tellurium (II) may also be coordinated with a tetradentate sulphur ligand. The sulphur-containing ligands may be either neutral or anionic.

Useful monodentate sulphur ligands include neutral Lewis base ligands such as thiourea and substituted thioureas such as ethylene thiourea, N,N′-diphenylthiourea, 1-(1-naphthyl)-2-thiourea, tetramethyl thiourea; 1-methyl-2-thiourea and 1-butyl-2-thiourea. Chelating thioureas, that is ligands containing one sulphur base site and a nitrogen base site are also useful. Suitable ligands of this type include 1-(2-pyridyl)thiourea; N-phenyl-N′-(5-halo-2-pyridyl) thiourea; 1-alkyl-3-(2-pyridyl)-2-thiourea; 1-phenyl-3-(2-pyridyl)-2-thiourea and amidino-2-thiourea. Other suitable ligands include the thioureas listed in the Eastman Organic Chemicals catalog #47 (1974) on page 322.

Useful bidentate sulphur ligands include anionic bidentate ligands such as thiosulphates, thiosulphonates, dithiocarbamates such as those having the formula $(R'_2NCS_2)^-$ wherein R′ is aryl such as phenyl or naphthyl, alkyl or cycloalkyl having 1-20 carbon atoms including methyl, propyl and isopropyl; cyclohexyl; xanthates such as those having the formula $(R^2OCS_2)^-$ wherein R^2 is alkyl or cycloalkyl having 1-20 carbon atoms (e.g. methyl, propyl, isopropyl and cyclohexyl); dithiophosphates such as those having the formula $((R^2O)_2PS_2)^-$; dithiophosphinates such as those having the formula $(R^2_2\ PS_2)^-$; dithiocarboxylates such as those having the formula $(R^3CS_2)^-$ wherein R^3 is aryl such as phenyl, naphthyl and substituted phenyl, or alkyl or cycloalkyl having 1-20 carbon atoms; substituted dithiaalkanes such as those having the formula $R^4\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}R^5$ wherein n is an integer from 1-6 and R^4 and R^5 are the same or different and are aryl such as phenyl, naphthyl, substituted phenyl. Other suitable 1,1 and 1,2-dithiobidentate ligands are described in D. Coucouvanis, *Prog. Inorg. Chem. 11*, 233 (1970).

Suitable tridentate sulphur-containing ligands include substituted trithiaalkanes such as those represented by the formula $R^4\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}R^5$ wherein R^4, R^5 and n are defined above; 1,1,1-tris(methylthiomethyl) ethane and 1,1,1-tris(phenylthiomethyl)ethane. Suitable tetradentate sulphur containing ligands include substituted tetrathiaalkanes such as those represented by the formula $R^4\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}R^5$ wherein R^4, R^5 and n are as defined above; and macrocyclic

thioether ligands such as those described in K. Travis and D.H. Busch, Inorg. Chem. *13* 2591 (1974).

Provided that at least one of the coordination positions of the tellurium (II) complex is occupied by a sulphur-containing ligand as described above, the remaining positions, if any, may be occupied by either neutral or anionic ligands. Depending on the chosen combination of sulphur containing ligands, neutral ligands and anionic ligands, the complexes used in the present invention may have a charge of from 0 to 2. Where a complex has a charge other than 0, a neutral salt of the complex is useful herein. Where the complex itself is neutral, it may be used alone. As used herein therefore the term "complex" is used to refer to both includes neutral complexes and salts of non-neutral complexes.

The particular neutral or anionic ligand that may be used, with the sulphur-containing ligand or ligands is not critical. Any of a wide variety of ligands known in the art may be used so long as such ligand is compatible with the sulphur ligand. Typical useful neutral ligands have group VA or VIA donor atoms. Examples of such ligands are $P(C_6H_5)_3$; 1,10-phenanthroline and 2,2'-bipyridine. Typical anionic ligands include halides such as chloro, bromo and iodo; ions which function like halides as $(NCO)^-$, $(NCS)^-$, $(NCSe)^-$ and $(NCTe)^-$; cyanoborohydrides such as $(BH_3CN)^-$; hydroborates such as $(BH_4)^-$, $(B_3H_8)^-$ and $(B_9H_{14})^-$; carboxylates such as $(CH_3CO_2)^-$ and $(CF_3CO_2)^-$, dicarboxylates such as $C_2O_4^=$, and $(NO_2)^-$; $(NO_3)^-$; $(SO_4)^=$; $(BF_4)^-$; $(B(C_6H_5)_4)^-$; $(ClO_4)^-$ and $(PF_6)^-$.

As discussed above, an extremely wide variety of coordination complexes of tellurium (II) are useful herein. A particularly useful group includes complexes wherein the tellurium (II) is complexed with two univalent bidentate sulfur containing ligands. The complexes of this group can be prepared by two general methods: 1) ligand reduction of a tellurium (IV) species in aqueous solution with excess of the bidentate sulfur ligand and 2) a substitution reaction using a tellurium (II) coordination complex with weakly bound ligands. In the first method, an especially convenient synthesis involves the formation of an aqueous solution of a tellurium (IV) halo complex by dissolving tellurium dioxide (TeO_2) in a warm aqueous hydrohalic acid solution followed by addition of the anionic bidentate sulphur ligand as its potassium or sodium salt. The bidentate sulphur ligand reduces tellurium (IV) to tellurium (II) and the excess ligand allows the formation of the desired tellurium (II) coordination complex which rapidly precipitates from the reaction solution. This crude product is filtered, washed well with water, dried and purified by recrystallization from an appropriate nonaqueous solvent. The reaction temperature used in such syntheses depends on the reducing properties of the bidentate sulphur ligand. For example with xanthates the reaction goes readily at room temperature, while with dithiocarbamates it is necessary to heat the solution for several minutes to effect complete reduction.

In the second method, an especially convenient tellurium (II) reagent for carrying out the substitution reaction is the thiosulfate complex $Na_2Te(S_2O_3)_2 \cdot 2H_2O$. This material can be readily prepared as described in O. Foss, Acta Chem. Scand., *3* 708 (1949). The thiosulphate ligands are very weakly bound in this complex and can be readily displaced in aqueous solution by the bidentate sulphur ligands described above. The neutral tellurium (II) complexes which precipitate from these reaction solutions can be isolated and purified as described above. Complexes wherein the tellurium (II) is complexed with two bidentate sulphur containing ligands may conveniently be represented by the general formula:

$$[Te(BL^1)\quad(BL^2)]$$

wherein BL^1 and BL^2 are the same or different and represent bidentate sulphur containing ligands as defined above. Typical complexes in this group include:

1. $[Te(S_2COC_2H_5)_2]$
2. $[Te(S_2P(C_6H_{11})_2)_2]$
3. $[Te(S_2COC_5H_{11})_2]$
4. $[Te(S_2COCH(CH_3)_2]$
5. $[Te(S_2CO\text{-}n\text{-}C_{10}H_{21})_2]$
6. $[Te(S_2CO\text{-}n\text{-}C_{12}H_{25})_2]$
7. $[Te(S_2P(OCH_3)_2)_2]$
8. $[Te(S_2P(OC_2H_5)_2)_2]$
9. $[Te(S_2O_2CH_3)_2]$
10. $[Te(S_2O_2C_6H_5)_2]$

A second particularly useful group includes complexes wherein the tellurium (II) is complexed with two monodentate ligands which are neutral Lewis bases and contain sulfur donor atoms and with two ligands which are univalent anionic ligands. These complexes may be prepared by methods well known in the art such as by ligand reduction of a tellurium (IV) complex using the appropriate sulfur ligand. Here, as described above, an especially convenient method of synthesizing these complexes is the reaction of the monodentate sulfur ligand with a tellurium (IV) halo complex prepared by dissolving tellurium dicoxide in the appropriate aqueous hydrohalic acid. The sulphur ligand, which is used in 5 to 10 fold excess, functions both as the reducing agent (i.e., tellurium (IV) → tellurium (II)) and as a stabilizing ligand for the tellurium product. Such ligand reduction reactions have been described for the synthesis of similar tellurium (II) coordination complexes (i.e., see O. Foss and S. Hauge, Acta Chem. Scand., *13*, 1252 (1959) and P. R. Sethuraman et al, Indian J. Chem., *11* 288 (1973)). Having formed the halo complex, the two halo ligands can be substituted via metathesis reactions by other anionic ligands such as SCN- or SeCN-. Generally the halo complex is isolated first and then added to a concentrated aqueous solution of an alkali metal salt of the desired anion and stirred at room temperature for 0.1-0.5 hr to effect the substitution reaction as described in O. Foss and S. Hauge, Acta. Chem. Scand., *13*, 1252 (1959); *15*, 1615 (1961). Complexes of this second group may conveniently be represented by the general formula:

$$[Te(NML^1)\ (NML^2)\ (UAL^1)\ (UAL^2)\ ]$$

wherein NML^1 and NML^2 are the same or different and represent neutral Lewis base monodentate ligands containing sulphur donor atoms as defined above, and UAL^1 and UAL^2 are the same or different and represent univalent anionic ligands as defined above. Typical complexes in this group are:

21. $[Te(thiourea)_2(Cl)_2]$
22. $[Te(thiourea)_2(SCN)_2]$
23. $[Te(1\text{-allyl-2-thiourea})_2(Cl)_2]$
24. $[Te(1,3\text{-diallyl-2-thiourea})_2(Cl)_2]$
25. $[Te(1\text{-naphthyl-2-thiourea})_2(Br)_2]$
26. $[Te(N\text{-phenylthiourea})_2Br_2]$
27. $[Te(1,3\text{-diallyl-2-thiourea})_2Br_2]$

A third particularly useful group includes complexes wherein the tellurium (II) is coordinated to four monodentate ligands which are neutral Lewis bases and contain sulphur donor atoms. All four ligands may be the same or there may be two of one ligand and two of another coordinated with the tellurium (II). These complexes have a charge of +2 and form salts with common anions. These complexes are formed by the same method as those of the second group above using a large excess of the desired sulfur ligand. Complexes of this third group may conveniently be presented by the general formula

$$[Te(NML^1)_2(NML^2)_2]\ (UAL^1)\ (UAL^2)$$

wherein NML^1, NML^2, UAL^1 and UAL^2 are as defined above. Typical complexes in this group are:

31. $[Te(1\text{-}(1\text{-naphthyl})\text{-2-thiourea})_4]Cl_2$
32. $[Te(thiourea)_4]Cl_2$
33. $[Te(ethylenethiourea)_4]Cl_2$

Of the preferred groups of complexes described above, complexes of the second and third groups are most useful in room temperature ligand development processes. Thus, these complexes may be included in a physical developer solution or may be incorporated in a catalytic nuclei containing material which is developd by treatment with a suitable solvent. Particularly useful complexes for use in these embodiments are:

$[Te(thiourea)_2Cl_2]$

$[Te(ethylenethiourea)_4]Cl_2$

$[Te(thiourea)_2(SCN)_2]$

$[Te(N\text{-}phenylthiourea)_2Br_2]$

Some of the complexes of the first group, that is complexes wherein the tellurium (II) is complexed with two bidentate sulphur ligands undergo thermal decomposition even in the absence of a solvent. Thus, they may be incorporated in a catalytic nuclei-containing material which is processed by the application of heat alone. Particularly useful complexes for use in this embodiment are:

11. $[Te(S_2COCH_3)_2]$
1. $[Te(S_2COC_2H_5)_2]$
12. $[Te(S_2CO\text{-}i\text{-}C_3H_7)_2]$
13. $[Te(S_2CO\text{-}n\text{-}C_{16}H_{33})_2]$
14. $[Te(S_2CO\text{-}n\text{-}C_{18}H_{37})_2]$
(15) $[Te(S_2COC_3H_5)_2]$
2. $[Te(S_2P(C_6H_{11})_2)_2]$
7. $[Te(S_2P(OCH_3)_2)_2]$
16. $[Te(S_2P(O\text{-}i\text{-}C_3H_7)_2)_2]$
8. $[Te(S_2P(OC_2H_5)_2)_2]$

Complexes of the first group above which undergo catalytic decomposition at about room temperature (print out) include complexes wherein the tellurium (II) is complexed with dithiophosphate such as $[Te(S_2P(OCH_3)_2)_2]$ and $[Te(S_2P(OC_2H_5)_2)_2]$. When incorporated in a dry imaging material these complexes form an image within a few seconds after imagewise exposure. No further development steps are necessary.

Formation of tellurium may take place by a classical disproportionation reaction which can be represented by the equation:

$$Te(II)COMPLEX \longrightarrow Te(O)+Te(IV)COMPLEX$$

or by ligand reduction of tellurium (II) which can be represented by the equation:

$$Te(II)COMPLEX \longrightarrow Te(O)+OXIDIZED\ LIGAND$$

Any method of producing nuclei of tellurium, palladium, silver or copper (or a mixture of two or more of these) is useful in the practice of this invention. Vacuum-deposited nuclei images alone can serve as catalytic nuclei for the reduction of the tellurium complexes to elementary tellurium. Compounds which are capable of producing these nuclei may be imagewise reduced, such as by a photoreductant, to form the nuclei. Numerous photosensitive compounds which are themselves capable of forming nuclei are also useful in producing the catalytic nuclei according to the present invention. Silver halide emulsions which comprise for example, silver chloride, silver bromide, silver bromoiodide, silver chlorobromide, silver chloroiodide, silver chlorobromoiodide crystals or mixtures thereof are useful herein. Useful techniques for production of silver halide emulsions and addenda for use therein are described in Product Licensing Index, Volume 92, December 1971, publication 9232, pages 107-110.

Palladium nuclei may be generated by the exposure of a wide variety of photosensitive palladium complexes as described, for example, in U.S. Patent 3,719,490; "Research Disclosure" items 13705, Sept. 1975, and 14229, Feb. 1976. Useful complexes include $(K_2Pd(C_2O_4)_2)$; $[Pd(P(C_6H_5)_3)_2C_2O_4]$; and $[Pd(1,1,7,7\text{-}tetraethyldiethylenetriamine)N_3](B(C_6H_5)_4)$.

Similarly, copper nuclei may be generated by the exposure of a wide variety of photosensitive copper complexes. Useful light sensitive copper complexes are described for example in U.S. Patents 3,859,092; 3,860,500; 3,860,501; and 3,880,724.

Useful complexes include:

$[Cu(P(OCH_3)_3)_4]B(C_6H_5)_4$

$[Cu(P(OCH_3)_3BH_3CN]_2$

$Cu(Sb(C_6H_5)_3)_2Cl$

$Cu(As(C_6H_5)_3)_3NO_3$

$Cu(As(C_6H_5)_3)_3BH_3CN \cdot CHCl_3$

$Cu(P(C_6H_5)_3)_2B_3H_8$

$Cu(P(p\text{-tolyl})_3)_2BH_4$

$[Cu(ethylenediamine)_2]\ (B(C_6H_5)_4)_2$

$[Cu(1,3\text{-propanediamine})_2]\ (B(C_6H_5)_4)_2$

According to preferred embodiments of the present invention, the tellurium (II) complex undergoes catalytic decomposition upon the application of heat or upon immersion in a solvent. In the first of these embodiments, an image is formed by heating the complex to a temperature sufficient to decompose the complex in the presence of catalytic nuclei but insufficient to decompose the complex in the absence of the nuclei. Development may be accomplished by heating to 75°C to 200°C, preferably 125°C to 175°C, for some 2 to 60 seconds. The time and temperature may vary with the specific catalyst and complex used and the optimum is easily determined by one skilled in the art. Sensitive sheet materials may be heated, for example, by passing them between heated rollers or by contacting them with a heated surface. In the second of these embodiments, the material containing the nuclei and tellurium complex is developed by contacting it with a suitable solvent. The solvent should be one in which the coordination complex is soluble and the visible image (tellurium (O)) is insoluble. Useful solvents include dimethylformamide, acetonitrile and alcohols such as methanol and ethanol. The material may be contacted, for example by dipping it in the solvent, by spraying it with the solvent, or by subjecting it to vapours of the solvent. The time of development can vary, for example, between 1 sec. and 60 sec. Development should be terminated before a significant amount of complex begins to develop in the non-exposed areas.

When the tellurium complex is to be the source of catalytic nuclei, a photoreductant may be incorporated to facilitate the formation of the tellurium nuclei. Since the photoreductant is incorporated to facilitate the production of the catalytic image, it need only be present in an amount less than that needed to reduce all of the tellurium complex to image substance. The photoreductant is preferably present at a concentration in the range of 0.5 to 50 milligrams per millilitre of the solution containing the tellurium complex. The preferred coverage of the photoreductant is from 0.5 to 100 mg per 0.093 m^2.

Any photoreductant can be used. Preferred photoreductants include quinone types with an internal hydrogen source for the hydroquinone formation. Other useful photoreductants are those of the quinone type which require a supplementary compound to supply hydrogen for the formation of the hydroquinone reducing agent. Photoreductants of these types are found in Tables 3 and 5 of U.S. Patent 3,880,659. Other useful photoreductants are described in U.S. Patents 3,881,930 and British Patents 1,373,546 and 1,281,565. Examples of preferred photoreductants are 4H-benzimidazoles, azidoquinones and 2-isopropoxy-1,4-naphthoquinone.

The photographic materials may contain any of a wide variety of conventional addenda such as thermal solvents, antifoggants and surfactants. Suitable addenda are described for example in Product Licensing Index, Vol. 92, pages 107-110, December, 1971.

Photographic materials of the present invention may utilize any common photographic support. Typical supports include cellulose nitrate film, cellulose acetate film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film, glass, paper, particularly when acylated or coated with baryta and/or an alpha-olefin polymer, and metal.

Materials useful according to the present invention may be prepared by causing a porous support to imbibe a solution of the photosensitive composition and/or tellurium complex. For example, a photosensitive material may be prepared by soaking porous paper in such a solution and drying.

Photographic materials of the invention containing both a tellurium complex and a

photosensitive compound can be prepared by incorporating both substances in a single coating composition. Alternatively, the substances may be coated in separate layers which are adjacent or are separated by a layer or layers that are sufficiently permeable to allow the necessary reactions to occur. When incorporated in the photographic material, the tellurium complex is preferably present in an amount between 5 mg and 250 mg/0.093 m^2.

A suitable coating composition for the tellurium complex includes the complex and a binder. Useful binders vary widely and include those binders ordinarily useful in silver halide photography. Since the materials of the present invention need not be processed in aqueous solutions, useful binding agents need not be water permeable, however they must be compatible with the tellurium complexes. By compatible it is meant that the binder must not react with the complex and, in the embodiments wherein the complex is itself photosensitive, the binder must transmit light to which the complex is sensitive. Illustrative binders include polyacetals such as poly(vinyl butyral) and poly(vinyl formal), cellulose esters, gelatin, and various vinyl polymers such as poly(vinylidene halides).

Physical developers containing the tellurium complex may be prepared. These developers are useful in processing materials having thereon the physically developable catalytic nuclei. Suitable solvents include those mentioned above for solvent development. The physical developers are prepared by simply dissolving the complex in the solvent at room temperature. Depending on the particular solvent-complex combination, these solutions are stable for from several hours to several days. When used in solutions as physical developers, the tellurium complexes are preferably present at a concentration of from 10 mg to 1 g per 100 millilitres.

The following examples are presented for a further understanding of the invention:

Example 1

Dichlorobis(thiourea)tellurium (II) was prepared by the addition of thiourea to a solution of $[TeCl_6]^{2-}$ in concentrated HCl as described in O. Foss and S. Hauge, Acta Chem. Scand., *13*, 1252 (1959). A solution of 100 mg of the yellow complex in 10 ml dimethylformamide (DMF) was dropped on a microscope slide on which a grid pattern of tellurium had been deposited by vapour deposition through a screen. The latent image areas containing tellurium nuclei immediately became visible on contact with the DMF solution of the complex. By use of a glass slide on which was evaporated a step tablet distribution of tellurium, the minimum coverage of tellurium necessary for initiation of this nonaqueous physical development process was found to be 0.125 mg/0.093 m^2.

The preparation of metallic nuclei vacuum-deposited step tablet distributions is described in J. F. Hamilton and P. C. Logel, Thin Solid Films, *23*, 89 (1974).

Example 2

A sensitized film containing $[TeCl_2(thiourea)_2]$ was prepared by coating a solution of 200 mg of the complex in 15 ml of a 5% DMF solution of Dow 'Saran' F-300 (trade mark for copolymer of vinylidene chloride and vinyl chloride) on unsubbed poly(ethylene terephthalate) (wet thickness of coating = 9 mil). This pale yellow film produced a visible image after a 20 minute exposure under a 360 watt Gates lamp (a high pressure mercury arc lamp 'Raymaster' Model 420-U1, G.W. Gates & Co.) at a distance of 12". This image could be subsequently amplified by heating for 30 seconds at 150°C.

Example 3

Sensitized stock was prepared by coating (9 mil wet thickness) a solution of 150 mg of $[TeCl_2(thiourea)_2]$ and 150 mg of the photoreductant 2-isopropoxy-1,4-naphthoquinone in 10 ml of a 5% DMF solution of Dow 'Saran' F-300 on unsubbed poly(ethylene terephthalate). The dried film contained 167 mg tellurium per 0.093 m^2.

A 60-second Gates lamp exposure of this film at a distance of 12" gave a faint visible image which was converted to a dark brown image on heating the exposed film for 30 seconds at 150°C. Exposures of this photothermographic imaging material with a grating monochromator at 375 nm followed by processing for 30 seconds at 150°C produced an image reflection density of 0.2 above fog for an exposure of about 5×10^5 ergs/cm^2.

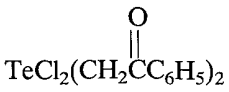
Example 4

The yellow complex $[Te(SCN)_2(thiourea)_2]$ was prepared by a metathesis reaction between $[TeCl_2(thiourea)_2]$ and KCNS. A solution of 100 mg of the complex in 5 ml of DMF was coated on poly(ethylene terephthalate) on which a series of steps of Pd nuclei had been deposited. All of the steps (lowest coverage = 0.0125 mg/ft^2) were immediately amplified to black visible images on contact with the solution of the Te(II) complex. Similar catalytic amplification was effected by vacuum deposited Te nuclei.

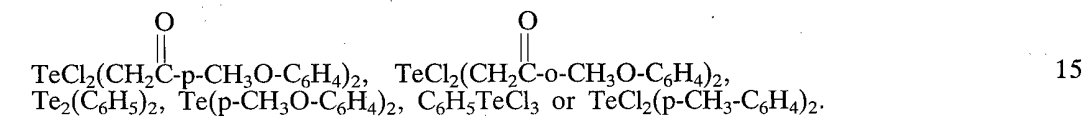
Example 5

This is a comparative example.

Example 4 was repeated with the exception that



was substituted for $[Te(SCN)_2(thiourea)_2]$. No image was formed when either vacuum evaporated palladium nuclei or tellurium nuclei coated on a poly(ethylene terephthalate) support were immersed in the solution. Similarly, no image was produced using



Example 6

Tellurium di(ethylxanthate) $[Te(S_2COC_2H_5)_2]$ was prepared as described in S. Huseby, Acta Chem. Scand., *21*, 42 (1967). A solution of 100 mg of the complex in 5 ml dichloromethane was coated on a glass microscope slide on which had been vacuum deposited a grid pattern of tellurium. Upon drying, the complex formed a pale yellow coating on the slide. When the slide was subsequently heated for 30 seconds at 175°C, the latent tellurium pattern was converted to a visible black grid pattern. A step tablet distribution of vacuum deposited palladium on poly(ethylene terephthalate) was prepared and coated with a solution of the Te(II) complex as described above. All the steps down to 0.056 mg Pd/ft^2 were readily amplified to visible images on thermal processing (30 sec., 150°C).

Example 7

A solution prepared by dissolving 100 mg $[Te(S_2COC_2H_5)_2]$ in 10 ml of a 4 per cent DMF solution of Poly(vinyl formal) was coated (9 mil wet thickness) on unsubbed poly(ethylene terephthalate). After a 3 minutes imagewise exposure with a 360 watt high pressure mercury lamp at a distance of 12″, a weak negative image was visible. Subsequent heating for 60 seconds at 135°C gave a dark brown negative image.

Example 8

Enhanced photographic response was obtained by incorporation of 100 mg of the photoreductant 2-isopropoxy-1,4-naphthoquinone in the coating solution of Example 7. Exposures of this sensitized film at 350 nm produced an image reflection density of 0.2 above background fog for an exposure of about 10^6 $ergs/cm^2$ with thermal processing for 60 seconds at 135°C.

Example 9

A solution of tellurium dioxide in concentrated hydrochloric acid was treated with a 4-fold molar excess of 1-allyl-2-thiourea in water. After concentration of the aqueous solution and dilution with ethanol a white product was crystallized out of the solution upon cooling. The product, which is insoluble in all common organic solvents but readily soluble in water, melts at about 190°C.

A solution of 100 mg of the white complex in 10 ml water was coated on a microscope slide on which had been vacuum evaporated a grid pattern of elementary tellurium. After drying, the slide was heated for 60 seconds at 190°C to produce amplification of the latent image tellurium depositions to visible black areas with no darkening in the areas on which tellurium had not been vacuum deposited.

Addition of 1,3-diallylthiourea to an aqueous solution of $[TeBr_6]^{2-}$ produced, after a similar workup as described above, a water soluble 1,3-diallythiourea complex of tellurium dibromide. This complex underwent tellurium catalyzed decomposition as described above for the 1-allyl complex.

Example 10

An aqueous solution (0.2 g/10 ml) of the 1,3-diallylthiourea complex of tellurium dibromide described in Example 9 was imbibed into a paper stock. After a 30-second imagewise exposure under a 360 watt high pressure mercury arc at a distance of 12″, a faint brown negative image formed. Subsequent heating of the exposed paper for 30 seconds at

160°C produced a brown negative image.

Example 11

A film sample containing $[Te(S_2COC_2H_5)_2]$ was prepared by dissolving 300 mg of the complex in 10 ml of a 4 percent solution of poly(vinyl formal) in dichloromethane. This solution was coated (9 mil wet thickness) on unsubbed poly(ethylene terephthalate) and dried. This film was then laminated with a strip of poly(ethylene terephthalate) on which had been vacuum evaporated silver nuclei (0.1 mg/0.093 m^2). The laminate, with the silver nuclei and tellurium (II) complex face-to-face, was then heated for 10 seconds at 145°C by passing through a photothermographic processor ('Cannon Kal' Developer). The heated sample blackened only in the area where the silver nuclei and tellurium complex were adjacent.

Example 12

The tellurium (II) coordination complex $[Te(1\text{-}(1\text{-naphthyl})\text{-}2\text{-thiourea})_4]Cl_2$ was prepared by reacting an aqueous solution of $[TeCl_6]^{2-}$ (i.e., TeO_2 + HCl) with excess 1-(1-naphthyl)-2-thiourea. The yellow precipitate was recrystallized from acetone-methanol. A solution of 100 mg of the complex in 10 ml DMF amplified vacuum evaporated tellurium nuclei in 2 minutes and vacuum evaporated silver nuclei in 3 minutes to visible images.

Example 13

Tellurium bis(diethyldithiophosphate) was prepared as described in S. Husebye, Acta Chem. Scand., *19*, 1045 (1965). The complex was recrystallized from hot ethanol to give orange crystals of the pure material. A solution of 100 mg of the complex in 5 ml of methylene chloride was imbibed into paper stock. Exposure of the resulting yellow coloured sensitized paper stock to heat from an 'Ascorlight' 660 Electronic Flash Unit (1 flash - the unit is sold by Berkey Technical Corp.) through a silver test negative gave a faint image which spontaneously amplified in about 60 seconds under ambient condition to a dark brown negative image.

Example 14

The complex $[Te(S_2P(C_6H_{11})_2)_2]$ (Complex 2) was prepared by the reaction of excess $NH_4^{\oplus}S_2P(C_6H_{11})_2^{\ominus}$ (ammonium salt of dicyclohexyldithiophosphinic acid) with $TeCl_6^{2-}$ (i.e., TeO_2 + HCl) in aqueous solution (4 moles of the ammonium salt:1 mole TeO_2). The crude product which precipitated from the aqueous reaction solution was filtered, washed with water, air dried and recrystallized from benzene to give dark red crystals of the pure product.

The utility of this tellurium (II) coordination complex as a physical developer for palladium and silver nuclei was evaluated using a film sample prepared by dissolving 100 mg of the complex in 8 ml of a 4-per cent chloroform solution of poly(vinyl formal) and coating this solution (9-mil wet thickness) on unsubbed poly(ethylene terephthalate). Lamination of this film sample face to face with poly(ethylene terephthalate) on which had been vacuum-deposited a step tablet distribution of metallic nuclei and subsequent heating of the sandwich for 30 seconds at 175°C amplified the metallic nuclei to a visible image.

Example 15

A sensitized paper was prepared by imbibition of a solution of 250 mg of the tellurium (II) complex $[Te(S_2P(C_6H_{11})_2)_2]$ in 10 ml benzene. After a 3-minute imagewise exposure of this sensitized paper stock with a 360 watt high pressure mercury arc (Raymaster 420-Ul), George W. Gates & Co.) at a distance of 12", it was amplified to a black negative image by heating for 30 seconds at 170°C.

A sensitized film sample was prepared by dissolving 100 mg of the complex and 100 mg of the naphthoquinone photoreductant described in Example 3 in 8 ml of a 4 per cent chloroform solution of poly(vinyl formal) and coating (9-mil wet thickness) on unsubbed poly(ethylene terephthalate). This film was given a 60 second imagewise exposure with the above mercury arc and then thermally developed (30 seconds, 175°C) to give a grey negative image.

Example 16

The complex $[Te(S_2COCH(CH_3)_2)_2]$ was prepared by the reaction of $Na_2Te(S_2O_3)_2 \cdot 2H_2O$ and $KS_2COCH(CH_3)_2$ in aqueous solution as described for the ethyl analogue in Example 6. The crude product was recrystallized from hot isopropanol-benzene (2:1) to give red needles of the pure product. The potassium isopropylxanthate was prepared by the addition of carbon disulphide to a solution of potassium hydroxide in isopropanol and the

crude product was recrystallized from isopropanol-water (4:1).

The palladium (O) and silver (O) catalyzed thermal decomposition of this complex was evaluated by coating a solution of the complex (50 mg/5 ml CH_2Cl_2) on the nuclei which had been vacuum-deposited in step tablet distributions on glass microscope slides. Subsequent heating of the coated slides for 10 seconds at 150°C produced amplification of the areas containing the nuclei to visible images.

Example 17

A dry tellurium amplification material was prepared in dissolving 250 mg of the tellurium complex of Example 16 in 15 ml of a 5 per cent chloroform solution of cellulose acetate butyrate and coating (9-mil wet thickness) on unsubbed poly(ethylene terephthalate). A sensitized film was prepared by dissolving 250 mg of $Cu[P(OCH_3)_3]_4 B(C_6H_5)_4$ (prepared as described in U.S. Patent 3,860,501) in 15 ml of 5 percent chloroform solution of cellulose acetate butyrate and coating (8-mil wet thickness) on unsubbed poly(ethylene terephthalate).

After a 15-second imagewise exposure of the above sensitized film under the mercury arc described in Example 15 it was laminated, face to face, with the above tellurium amplification material and passed through a set of heated rollers for 5 seconds at 140°C. A dark brown negative image resulted on the sensitized film.

Example 18

The compound $[Te(S_2COC_5H_{11})_2]$ was prepared by the general method described for the isopropyl analog in Example 6. The crude product was recrystallized from n-butanol-benzene (75°C, 4:1) to give orange needles of melting point 51°C.

A film sample containing this tellurium (II) complex was prepared by dissolving 100 mg of the complex in 10 ml of a 5-per cent chloroform solution of cellulose acetate butyrate and coating the solution on unsubbed poly(ethylene terephthalate) (9-mil wet thicknesses). Lamination of this film with poly(ethylene terephthalate) on which had been vacuum-deposited a step tablet distribution of palladium nuclei and passage of this sandwich configuration through heated rollers at 160°C for 5 seconds resulted in amplification of the palladium nuclei to a visible image.

Imagewise exposure of the above tellurium containing film for 30 seconds with the mercury arc described in Example 15 produced no visible image but subsequent heating of this exposed film for 10 seconds at 150°C produced a brown negative image.

Example 19

A sensitized film was prepared by dissolving 250 mg of the tellurium (II) complex $[Te(S_2COCH(CH_3)_2)_2]$ and 250 mg of the photoreductant described in Example 3 in 15 ml of a 2% chloroform solution of cellulose acetate butyrate and coating the resulting solution (9-mil wet thickness) on unsubbed poly(ethylene terephthalate). This film was then given a one flash exposure through a silver test negative with the electronic flash unit described in Example 13 at a distance of 3″. Subsequent heating of the exposed film at 150°C for 5 sec. gave a dark brown negative image.

Example 20

The complex $Te(S_2COC_{12}H_{25})_2$ was prepared by an analogous reaction to that described in Example 6 for the ethyl analog using $KS_2COC_{12}H_{25}$. The crude product was recrystallized from isopropanol-benzene (2:1) to give yellow orange needles having a mp of 81°C.

An imaging material containing this complex was prepared by dissolving 100 mg of the complex in 10 ml of a 4% methylene chloride solution of cellulose acetate butyrate and coating this solution (10 mil wet thickness) on poly(ethylene terephthalate). Exposure of this film for 5 min. under the mercury arc described in Example 2 gave a faint grey printout. Processing for 30 sec. at 150°C gave a black negative image.

Incorporation of 100 mg of the photoreductant 2-isopropoxy-1,4-naphthoquinone in the above coating solution results in enhanced photosensitivity of the imaging layer. With the photoreductant in the coating, the exposure time was reduced from 5 minutes to 30 seconds to give similar images under the processing conditions described above.

Example 21

The complex $Te(S_2COC_{18}H_{37})_2$ was prepared by an analogous reaction to that described in Example 6 for the ethyl analog using $KS_2COC_{18}H_{37}$. The crude product upon recrystallization from toluene gave a yellow solid having a mp of 76°C.

An imaging material containing this complex was prepared by dissolving 100 mg of the complex and 100 mg of the photoreductant 2-isopropoxy - 1,4-naphthoquinone in 25 ml of a

4% methylene choride solution of cellulose acetate butyrate with warming. This solution was coated (10 mil wet thickness) on poly(ethylene terephthalate). Exposure of this sensitized film for 60 sec. with the mercury arc described in Example 2 followed by thermal processing for 30 sec. at 145°C gave a black negative image.

Example 22

The complex bis(allylxanthato)tellurium (II) (Complex 15) was prepared by the general procedure described in Example 6 using $KS_2COC_3H_5$. The crude product was recrystallized from methylene chloride-ethanol (1:1) to give a crop of red orange needles.

A solution of 100 mg of this complex dissolved in 10 ml of CH_2Cl_2 was imbibed into paper stock. After a 30 sec. imagewise exposure of this sensitized paper stock with the mercury arc described in Example 2 and subsequent thermal processing for 30 sec. at 155°C a brown negative image was obtained.

WHAT WE CLAIM IS:-

1. A method of making a visible image which comprises forming an imagewise distribution of nuclei of tellurium, palladium, silver, copper or a mixture of two or more of these, and employing said distribution to catalyze the decomposition of a coordination complex of tellurium (II) in which at least one ligand contains a sulphur atom by which it is coordinated to the tellurium atom.

2. A method according to Claim 1 wherein the complex contains two univalent bidentate sulphur-containing ligands.

3. A method according to Claim 2 wherein the complex is one of the complexes 1 to 16 specified herein.

4. A method according to Claim 1 wherein the complex contains two monodentate Lewis base ligands having sulphur donor atoms and two univalent anionic ligands.

5. A method according to Claim 4 wherein the complex is one of the Complexes 21 to 27 specified herein.

6. A method according to Claim 1 wherein the complex is a salt which contains four monodentate Lewis base ligands having sulphur donor atoms, all four ligands being the same or there being two of each of two ligands present.

7. A method according to Claim 6 wherein the complex is one of the Complexes 31 to 33 specified herein.

8. A method according to any of the preceding Claims wherein the imagewise distribution of nuclei is formed by imagewise exposure of a layer of a radiation-sensitive compound or mixture of compunds.

9. A method according to Claim 8 wherein the nuclei are of tellurium and the radiation-sensitive compound is the tellurium (II) coordination complex.

10. A method according to Claim 8 or 9 wherein a photoreductant is present with the radiation-sensitive compound or mixture of compounds.

11. A method according to Claim 8 wherein the nuclei are of silver and the radiation-sensitive-compound is a photographic silver halide.

12. A method according to any of Claims 1 to 7 wherein the imagewise distribution of nuclei is formed by imagewise exposure of a photoreductant in the presence of a radiation-insensitive reducible compound or a mixture of such compounds.

13. A method according to Claim 12 wherein the nuclei are of tellurium and the radiation-insensitive reducible compound is a tellurium (II) complex.

14. A method according to any of Claims 1 to 7 wherein the imagewise distribution of nuclei is formed by vacuum evaporation on a support.

15. A method according to any of Claims 8 to 13 wherein the tellurium (II) complex is decomposed by heating in the presence of the nuclei.

16. A method according to any of Claims 8 to 14 wherein the tellurium (II) complex is applied as a solution to the imagewise distribution of nuclei.

17. A method according to any of Claims 8 to 13 wherein the tellurium (II) complex is decomposed by applying an organic solvent which can dissolve the complex to a layer or layers containing the complex and the imagewise distribution of nuclei.

18. A method according to Claim 1 substantially as described in any of Examples 1 to 4 and 6 to 22.

19. A sheet material which comprises a support coated on one side with a layer containing a tellurium (II) complex as defined in Claim 1 and a binder.

20. A material according to Claim 19 which contains a photoreductant incorporated in the layer containing the tellurium (II) complex or a binder-containing layer adjacent thereto.

21. A material according to Claim 19 which contains a radiation-sensitive palladium, silver or copper compound in the layer containing the tellurium (II) complex or a binder-containing layer adjacent thereto.

22. A coating composition which comprises a solvent dispersion of a tellurium (II) complex as defined in Claim 1 and a binder.

23. A method of making a sheet material which comprises coating a support with a layer of a coating composition according to Claim 22.

24. A material according to any of Claims 19 to 21 substantially as described in any of Examples 2, 3, 7, 8, 11, 14, 15 and 17 to 21.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,from
which copies may be obtained.