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3,690,886

PRINT-OUT PROCESS UTILIZING CHEMICALLY SENSITIZED LEAD SALT IN ORGANOPHILIC BINDER

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11 Claims

ABSTRACT OF THE DISCLOSURE

A print-out recording method and material using a recording layer comprising a photosensitive lead halide salt dispersed in an organophilic binder. Preferred lead salts are lead iodide, lead bromide, or a crystalline mixture thereof. A sensitizing agent may be added to increase the photosensitivity of the lead salt. Faint print-out images may be intensified by treatment with a physical development using, for instance, a solution containing a reducing agent and metal ions of a metal more electro-positive than lead.

The present invention relates to photographic materials suited for image formation by "printing-out" and that are of the non-silver halide type.

The formation and development of latent silver images is generally known. The replacement of silver by other metals has been made the object of an intensive research in order to lower the cost of the photographic materials.

Among photo-sensitive metal compounds other than silver compounds lead compounds such as lead iodide, lead azide or lead bromide have proved to be valuable as described, e.g., in the U.S. patent specification 2,414,839.

It has now been found that contrary to what is known in the preparation of photo-sensitive silver halide materials photosensitive lead salts, preferably lead iodide and lead bromide offer a valuable "print-out" sensitivity when dispersed in an organophilic binder or binder system. So, the present invention provides a new photosensitive recording material comprising a photosensitive lead salt such as lead bromide, lead iodide or a crystalline mixture of lead iodide and lead bromide dispersed in an organophilic binder or binder system.

By the term "organophilic binder or binder system" is meant a binding agent or mixture of binding agents, which is soluble in an organic solvent, e.g. alcohols preferably lower alcohols such as methanol and ethanol, aliphatic carboxylic acid esters and aliphatic ketones.

By the term "print-out" is meant the formation of a visible image by exposure to active radiation including electromagnetic radiation and ionizing radiation, e.g. β -radiation, without the aid of a further development.

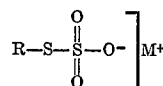
The exposure of the photosensitive article according to the present invention may proceed in dry or wet state. Wetting preferably occurs with a lower aliphatic alcohol, e.g. methanol.

The lead salts can be sensitized by means of so-called chemical sensitizers. A first group of these sensitizing agents are sulphur compounds or compounds wherein sulphur has been replaced by selenium or tellurium. Preferably those sulphur, selenium or tellurium compounds are used that possess reducing properties and/or that contain a releasable sulphur, selenium or tellurium atom, i.e. a sulphur, selenium or tellurium atom that is easily split

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off e.g. by heating. In that respect are to be mentioned particularly compounds selected from the group consisting of:

- (1) thiol compounds or thiolates,
- (2) compound corresponding to the following structural formula:

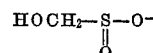


wherein:

M^+ represents a cation, e.g. a hydrogen ion, metal ion or onium group, which is missing when the radical R already contains a cationic residue (betaine type compound), and

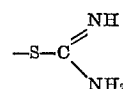
R represents an organic group, e.g. an alkyl, aryl or heterocyclic group including said groups in substituted form (see for specific compounds e.g. the United Kingdom patent specifications 997,031 and 1,157,172)

- (3) compounds yielding HSO_3^- ions,
- (4) compounds yielding SO_3^- ions,
- (5) compounds yielding



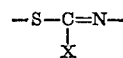
ions, $\text{M}-\text{O}-\text{S}-\text{O}^-$ ions, wherein M is a cation, or SO_2^- ions derived from the hypothetical sulfoxylic acid $\text{S}(\text{OH})_2$

- (6) compounds yielding $\text{R}-\text{SO}_2-\text{S}^-$, R.CO.S^- , R.CS.S^- or R.SC.O^- ions, wherein R is an organic group, e.g. an alkyl group such as a methyl group, a substituted alkyl group, an aryl group or a substituted aryl group,
- (7) compounds yielding S^- ions or $\text{M}-\text{S}^-$ ions, wherein M is a cation,
- (8) compounds yielding S_2O_4^- ions,
- (9) compounds yielding SCN^- ions,
- (10) organic isothiocyanates,
- (11) compounds containing a



group,

- (12) compounds containing a $\text{a} > \text{P}=\text{S}$ group,
- (13) compounds containing a $-\text{S}-\text{S}-$ group,
- (14) compounds containing a $-\text{S}-\text{S}_x-$ group, wherein $x > 2$
- (15) compounds containing a homopolarly bound $-\text{S}-\text{R}_1$ group, wherein R_1 is an organic group, linked through a carbon atom to the sulphur atom, e.g. an acyl, an alkyl, an aryl or a heterocyclic group,
- (16) compounds containing a

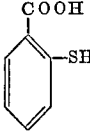
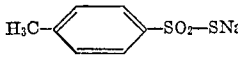
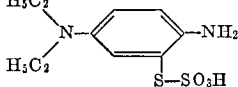
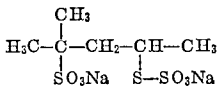
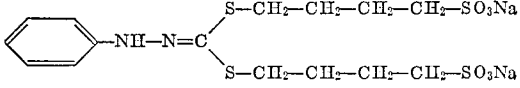
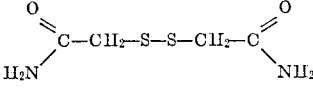


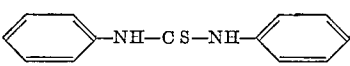
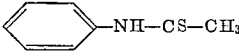
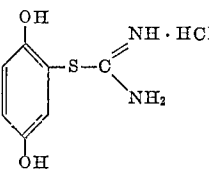
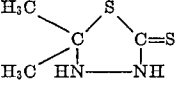
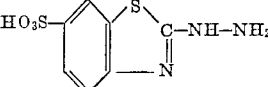
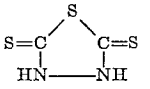
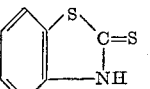
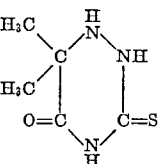
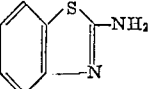
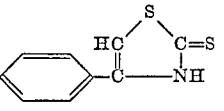
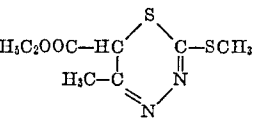
group, wherein X is an amino or hydrazino group and said sulphur containing group makes part of a heterocyclic ring or ring system,

- (17) compounds of As, Sb or Sn, known as thiosalts, e.g. K_3AsS_4 , KAsS_3 , $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ and K_2SnS_3 ,
- (18) compounds containing a $> \text{C}=\text{S}$ group,
- (19) compounds yielding S_2O_3^- ions,
- (20) xanthates, i.e. salts of xanthic acid having the general formula $\text{R}_2\text{O.CS.SM}$, wherein M is a cation, e.g. an alkali metal cation, and R_2 is an alkyl or substituted alkyl radical, e.g. a benzyl radical.

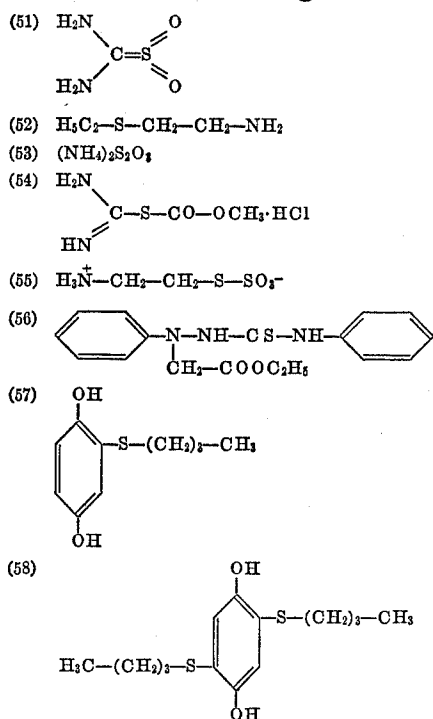
Particularly useful sulphur-containing chemical sensitizing agents are the compounds enumerated in the following table.

TABLE 1

- (1) $\text{O}=\text{S}-\text{ONa}$
 $\quad \quad \quad |$
 $\quad \quad \quad \text{CH}_2\text{OH}$
 or $\text{HCHO} \cdot \text{NaHSO}_3 \cdot \text{H}_2\text{O}$ (sold under the trade name Rongalit)
- (2) $\text{Na}_2\text{S}_2\text{O}_3$
- (3) $\text{Na}_2\text{S}_2\text{O}_4$
- (4) $\text{Na}_3\text{OsS}_4 \cdot 8\text{H}_2\text{O}$
- (5) P_2S_5
- (6) KSCN
- (7) NaHSO_3
- (8) NH_4SCN
- (9) $\text{HS}-\text{CH}_2-\text{COOH}$
- (10) $\text{HS}-\text{CH}_2-\underset{\text{SH}}{\text{CH}}-\text{CH}_2-\text{OH}$
- (11) CH_2-COOH
 $\quad |$
 $\text{CH}-\text{COOH}$
 $\quad |$
 SH
- (12) 
- (13) 
- (14) 
- (15) $\text{NaO}_3\text{S}-\text{S}-\text{CH}_2\text{COONa}$
- (16) $\text{H}_3\text{C}-(\text{CH}_2)_{15}-\text{S}-\text{SO}_2\text{Na}$
- (17) $\text{NaO}_3\text{S}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}-\text{SO}_2\text{Na}$
- (18) $\text{C}_2\text{H}_5-\text{SO}_2-\text{SK}$
- (19) 
- (20) $\text{KO}_3\text{S}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SCN}$
- (21) $\text{C}_2\text{H}_5\text{O}-\text{P}(=\text{S})(\text{C}_2\text{H}_5)_2$
- (22) $\text{H}_3\text{C}_2\text{O}-\text{P}(=\text{S})(\text{NH}_2)(\text{C}_2\text{H}_5)$
- (23) 
- (24) 
- (25) $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2 \cdot 2\text{HCl}$
- (26) $\text{S}=\text{C}-\text{OC}_2\text{H}_5$
 $\quad |$
 $\quad \text{SK}$

- (27) $\text{H}_3\text{C}-\text{CO}-\text{S}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{Na}$
- (28) 
- 5 (29) 
- (30) $\text{H}_3\text{C}-\text{CS}-\text{NH}_2$
- (31) $\text{H}_2\text{N}-\text{CS}-\text{NH}_2$
- 10 (32) $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{NH}-\text{CS}-\text{NH}_2$
- (33) $\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{S}-\text{C}(=\text{NH})\text{NH}_2 \cdot \text{HCl}$
- 15 (34) 
- 20 (35) $\text{H}_2\text{N}-\text{CS}-\text{NH}-\text{NH}_2$
- 25 (36) $\text{H}_3\text{C}_2\text{OOC}-\text{CH}_2-\text{CH}_2-\text{S}-\text{C}(=\text{NH})\text{NH}_2 \cdot \text{HCl}$
- (37) $\text{H}_2\text{N}-\text{CS}-\text{NH}-\text{NH}-\text{CS}-\text{NH}_2$
- 30 (38) 
- (39) 
- 35 (40) 
- 40 (41) 
- 45 (42) 
- 50 (43) 
- 55 (44) 
- 60 (45) 
- 65 (46) $\text{H}_3\text{C}-\text{CO}-\text{NH}-\text{CS}-\text{NH}_2$
- 70 (47) $\text{H}_2\text{N}-\text{CS}-\text{CS}-\text{NH}_2$
- (48) $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{SH}$
- (49) $\text{H}_3\text{C}-\text{SO}_2-\text{S}-\text{CH}_3$
- 75 (50) $\text{C}_2\text{H}_5\text{SCl}$

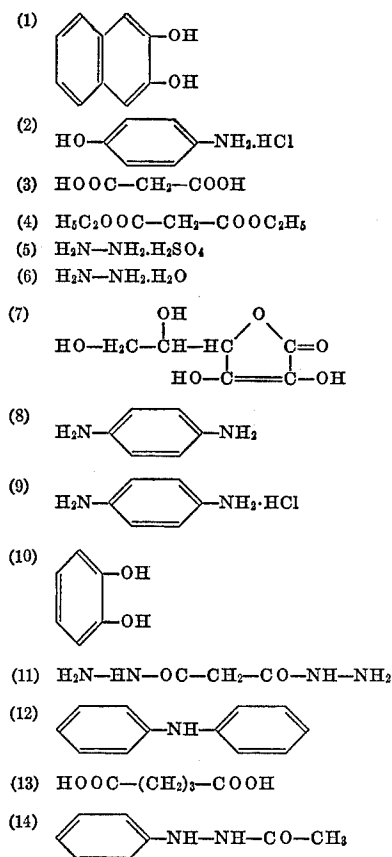
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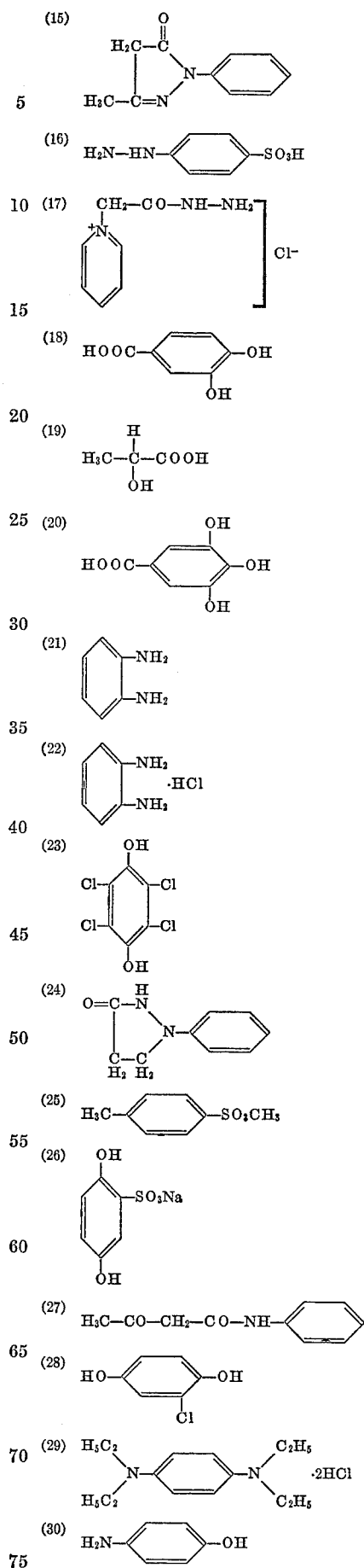
As selenium and tellurium compounds are particularly mentioned allyl selenourea and allyl telluourea. Further are mentioned selenium and tellurium compounds that as to their structure are derived from oxyacids, wherein one or more of the oxygen atoms has (have) been replaced by selenium or tellurium atoms.

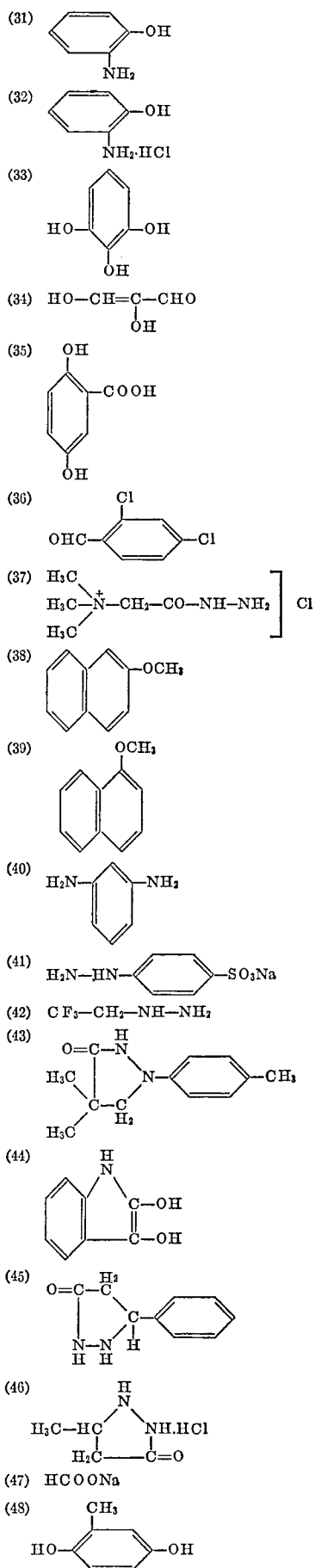
A second group of suitable chemical sensitizing agents are listed in the following Table 2.

TABLE 2

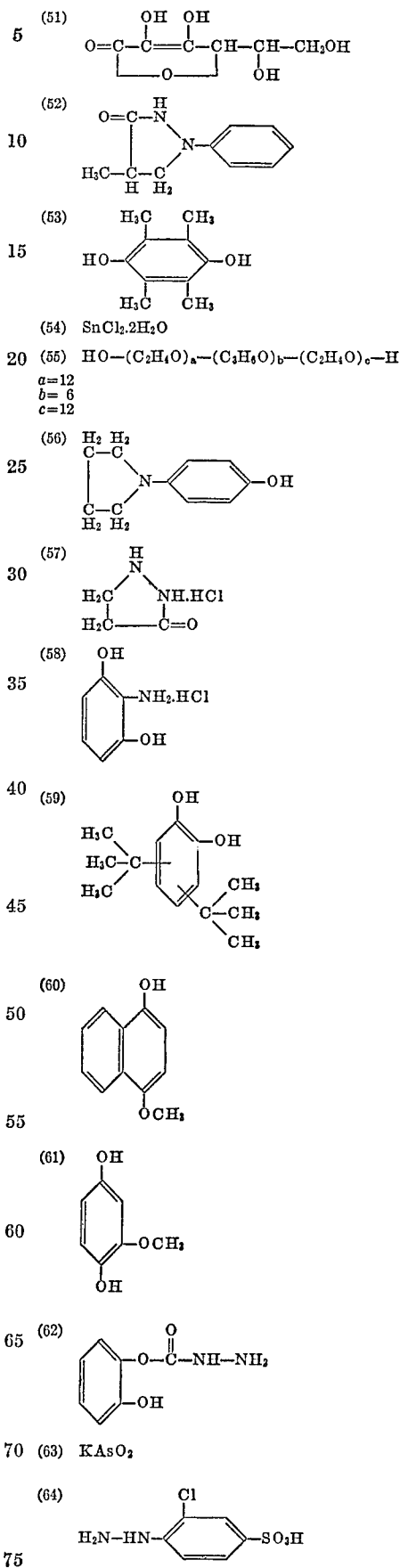


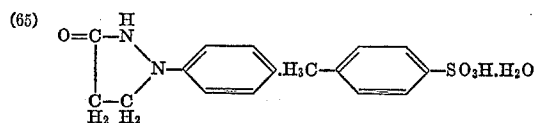
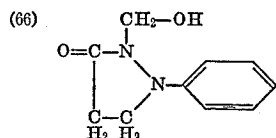
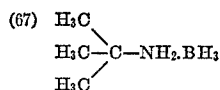
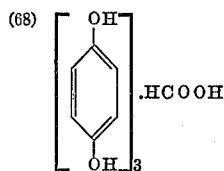
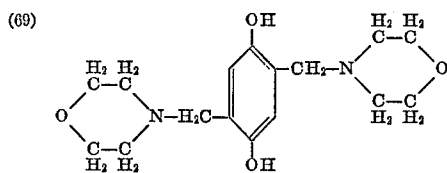
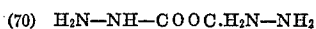
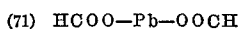
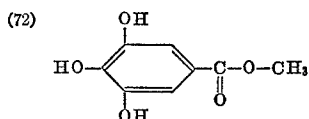
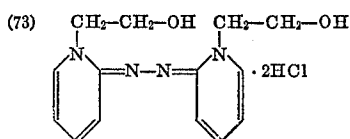
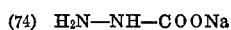
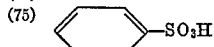
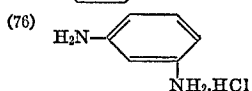
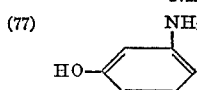
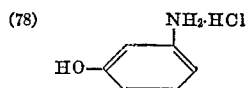
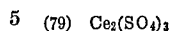
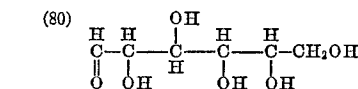
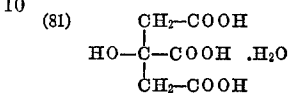
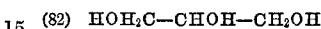
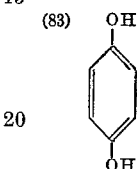
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(49) Tin(II) chelate of ethylenediamine tetraacetic acid
(50) Titanium(III) chelate of ethylenediamine tetraacetic acid



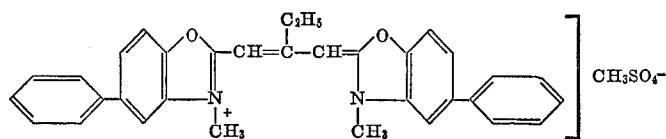


The light-sensitive compounds may be treated with the chemical sensitizers before, at the same time of or after coating the photosensitive composition to a support. Preferably they are added to the coating composition before coating and intimately mixed therewith, so that a chemical interaction can take place already before coating and storage. According to a particular embodiment the recording material is exposed while still being wet after the treatment with a solution containing a chemical sensitizing agent.

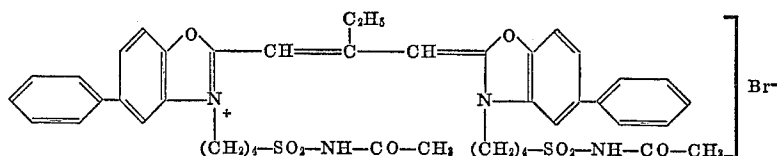
The chemical sensitizing agents may be used in a rather large amount, e.g. in a ratio by weight up to 1:2 in respect of the light-sensitive lead salt, preferably in a range of 1:100 to 1:1.

The photosensitive lead salts such as lead iodide or lead bromide are inherently sensitive to ultra-violet rays. By dye sensitization the said compounds can be made sensitive to light of the visible spectral region, so that they can yield a print-out or developable latent image by exposing it with the light emitted by a tungsten filament lamp or a flash lamp mainly emitting in the visible spectrum region.

For the purpose of spectral sensitization in the visible light spectrum cyanine dyes can be used e.g. the dyes having the formulae:



and



As organophilic binding agents particularly suited for use according to the present invention are mentioned sucrose benzoate and poly(vinyl-butyril), ethylcellulose, shellac, polyvinyl stearate, copoly(vinyl acetate/N-vinylpyrrolidone), and copoly(methacrylic acid/methyl methacrylate). The ratio by weight of binding agent or mixture of binding agents to light-sensitive lead salt is preferably between 9:1 and 1:3. The amount of light-sensitive lead salt per sq. m. can vary within wide limits but preferably amounts to at least 1 g. per sq. m.

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The preferably used lead iodide and lead bromide can be freshly prepared in finely divided state from a water-soluble lead compound, e.g. lead acetate, and a halide ion-releasing compound, e.g. sodium iodide. The precipitate of light-sensitive lead salt is freed from water before use. Mixtures of light-sensitive lead salts (crystalline mixtures), can be prepared by coprecipitation.

The grain size of the applied lead salts is preferably between 0.03 and about 10 micron.

The organic solvents used in the application of the coating composition are preferably anhydrous, although they may be polar or miscible with water such as methanol. The boiling point of said solvents is preferably not higher than 100° C. in order to enable an easy removal of the solvent after the recording layer has been coated.

When the lead salts are not spectrally sensitized the print-out images are relatively stable to daylight. They can be stored for at least two weeks in dimmed daylight. The stability in daylight can be increased by applying to the print-out images U.V. light-absorbing substances.

The recording materials of the present invention are suitable for the reproduction of line work as well as for the reproduction of continuous tone originals and for the recording of signals as are obtained from modulated spot recording systems and recording systems wherein penetrating rays such as X-rays, beta-rays or gamma-rays are applied.

If a water-permeable binding agent, e.g. ethyl-cellulose or polyvinyl-n-butylal, is used, an image-intensification technique may be applied. In other words too weak a print-out image, which has to be considered as a latent image, can be developed and made clearly visible by means of an aqueous liquid, which may contain a water-miscible organic solvent. For that purpose a so-called physical developer may be used.

The intensification or development of the latent image by means of a redox-system containing a reducing agent and ions of a metal that is more electropositive than lead and/or ions e.g. of dyestuffs or leuco compounds having a redox potential not lower than that of said ions is called here a physical development. So, the development can be carried out with ions of methylene blue, silver ions, mercury(II) ions, mercury(I) ions, copper(II) ions or copper (I) ions in the presence of a reducing agent, e.g. p-aminophenol, 1-phenyl-3-pyrazolidinone or ascorbic acid.

According to a simple physical development process the latent image, which according to some theoretical considerations is presumed to consist of lead or lead sulphide nuclei, is successively treated with a silver nitrate solution and a solution containing a reducing agent for silver ions. The silver image obtained in this way is fixed or stabilized. The stabilization, which in principle consists of the conversion in the recording material of light-sensitive salts in non-light-sensitive salts, may be effected by a short treatment (2 or 3 sec.) with an aqueous solution containing thiosulphate ions, e.g. originating from sodium thiosulphate, or with isothiocyanate ions, e.g. originating from sodium isothiocyanate.

Other suitable stabilizing compositions contain dissolved halide ions e.g. originating from ammonium fluoride and ammonium chloride, and/or contain a water-soluble carboxylic acid e.g. acetic acid.

The stabilizing or fixing solutions may contain water-soluble sulphites or hydrogen sulphites to prevent yellowing of the fixed image by oxidation of the developer.

Fixation may be carried out by treating the physically developed material for a larger time than in stabilization with a solution containing ammonium chloride and thiosulphate ions or other known silver ion-complexing agents dissolving the light-sensitive salts and transferring them to the fixing bath.

In the physical development the more electropositive metal ions and the reducing agent are preferably kept in separate solutions in order to avoid alteration of the developing bath.

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Contrary to classical silver halide emulsion developers, the physical developing composition need not to be alkaline. So, the pH thereof will preferably be kept below 7.

Suitable developing compositions for physical development are described in the Belgian patent specification 662,491 and the United Kingdom patent specification 1,043,250.

In order to improve the penetrating power of the developing solution it may contain wetting agents and water-miscible organic solvents, e.g. ethanol, ethylene glycol and non-ionic, anionic or cationic surfactants.

The following examples illustrate the present invention.

EXAMPLE 1

60 g. of sucrose benzoate and 75 g. of lead(II) bromide were ball-milled for 12 h. in 190 g. of methanol. The suspension obtained was then diluted with 300 g. of methanol and in a proportion of 100 g./sq.m. applied to a support. After drying, the light-sensitive material thus obtained was exposed for 60 sec. through a transparent negative by means of a Philips HP 80 lamp placed at a distance of 25 cm. A greyish-black positive copy on white background was obtained.

EXAMPLE 2

20 g. of poly(vinyl-n-butylal) and 75 g. of lead(II) bromide were ball-milled for 12 h. in 230 g. of methanol. To the suspension thus obtained a solution of 15 g. of Rongal HT type 66 (trade name of Badische Anilin- & Soda-Fabrik, Ludwigshafen, Germany, for the addition product of formaldehyde and sodium dithionate) in 300 g. of methanol was added. The suspension formed was applied in proportion of 110 g./sq.m. to a paper support. After drying, the material was image-wise exposed for 15 sec. by means of a 150 w. xenon lamp placed at a distance of 5 cm. A greyish-black copy on white background was obtained.

EXAMPLE 3

40 g. of poly(vinyl-n-butylal) and 150 g. of lead(II) iodide were ball-milled for 12 h. in 460 g. of methanol. To the suspension obtained a solution was added of 30 g. of mercaptoacetic acid in 350 g. of methanol. The suspension formed was applied to a paper support at a rate of 100 g. per sq.m. After drying, the material was exposed through a transparent negative in a Buroza 600 apparatus (trade name of Atlas, Delft, Netherlands, for a diazoprint apparatus), at a travelling speed of 30 cm./min. A greyish-black positive print-out copy was obtained on a yellow background.

EXAMPLE 4

40 g. of poly(vinyl-n-butylal) and 150 g. of lead(II) bromide were ball-milled for 12 h. in 460 g. of methanol. The suspension obtained was then applied to a paper support at a rate of 100 g./sq.m. After drying, this material was dipped in a 2% solution of 2,3-dimercapto-1-propanol in methanol, and when still wet exposed image-wise for 60 sec. by means of a Philips HP 80 lamp. A greyish-black image on a white background was obtained.

EXAMPLE 5

40 g. of poly(vinyl-n-butylal) and 150 g. of lead(II) bromide were ball-milled for 12 h. in 360 g. of methanol. The suspension obtained was diluted with 350 g. of methanol and coated onto a paper base in a proportion of 50 g. per sq.m. After drying, the material was exposed through a transparent negative in a Buroza 600 (trade name) diazo printing apparatus at a traveling speed of 8 cm./sec. The exposed material showing no visible image was successively dipped in the following baths:

(a) 10 sec. in a solution of 5 g. of silver nitrate in 85 ccs. of demineralized water and 10 ccs. of methanol

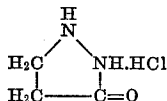
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- (b) 10 sec. in a solution of 2 g. of p-methyl-aminophenol sulphate, 88 ccs. of demineralized water and 10 ccs. of methanol, and
 (c) 5 sec. in a 10% solution of acetic acid in demineralized water.

After rinsing and drying, the material showed a positive brown silver image.

EXAMPLE 6

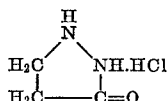
40 g. of poly(vinyl-n-butyral) and 150 g. of lead(II) iodide were ball-milled for 12 h. in 460 g. of methanol. To the suspension obtained a solution was added of 25 g. of the compound of the formula:



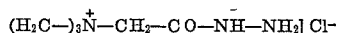
in 320 g. of methanol. This suspension was applied to a paper support so that 95 g. of lead(II) iodide were present per sq.m. After drying, the material was exposed through a transparent negative in a Buroza 600 (trade name) apparatus at a travelling speed of 20 cm./min. A black print-out image was obtained on a yellow background.

EXAMPLE 7

Example 6 was repeated with the proviso, however, that the compound of the formula:



was replaced by the same amount of compound of the formula:



Here also a black print-out image was obtained.

EXAMPLE 8

150 g. of lead(II) bromide were ball-milled for 12 h. in a solution containing 34 g. of poly(vinyl-n-butyral) and 6 g. of poly(N-vinylpyrrolidone) in 460 g. of methanol. To the suspension obtained a solution was added containing 2 g. of 1-ascorbic acid and 1 g. of citric acid in 32 g. of methanol. This suspension was applied to a paper support in a proportion of 150 g./sq.m. After drying, the light-sensitive material obtained was image-wise exposed in a Buroza 600 (trade name) apparatus at a copying speed of 2 cm./sec. The exposed material showing only a faint image was then successively dipped in the following baths:

- (a) 50 sec. in a solution of 5 g. of silver nitrate and 5 g. of citric acid in 90 ml. of demineralised water
 (b) 3 min. in a solution of 200 g. of sodium thiosulphate-5-water and 25 g. of potassium disulphate ($\text{K}_2\text{S}_2\text{O}_8$) in 775 ml. of demineralised water
 (c) 3 min. in running water.

After drying, a brown-black silver image was obtained.

EXAMPLES 9-18

40 g. of poly(vinyl-n-butyral) and 1500 g. of lead(II) bromide were ball-milled for 12 h. in 4600 g. of methanol. The obtained suspension was divided in 10 equal parts. To 9 parts thereof a solution was added of 3 g. of a sensitizing agent as listed below in 32 g. of methanol.

The different suspensions obtained were applied to a paper support in such a way that 26 g. of lead(II) bromide were present per sq.m. After an image-wise exposure in a Buroza 600 (trade name) apparatus at a

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travelling speed of 20 cm./min., the following print-out densities were recorded when measured by reflected light.

Example	Sensitizing agent	D_{max}	D_{min}
9	No addition	0.31	0.13
10	3 g. of 1-ascorbic acid	0.68	0.16
11	3 g. of 1-phenyl-3-pyrazolidinone	0.66	0.13
12	3 g. of gallic acid	0.72	0.15
13	3 g. of d-isoascorbic acid	0.64	0.14
14	3 g. of monochlorohydroquinone	0.55	0.13
15	3 g. of sodium salt of hydroquinone-sulphonic acid	0.60	0.13
16	3 g. of benzene sulphonic acid	0.70	0.20
17	3 g. of methyl-p-toluene-sulphonate	0.79	0.16
18	3 g. of $\text{H}_2\text{N}-\text{NH}-\text{COOH} \cdot \text{H}_2\text{N}-\text{NH}_2$	0.59	0.14

EXAMPLE 19

4 g. of poly(vinyl-n-butyral) and 15 g. of lead(II) iodide were ball-milled for 12 h. in 46 g. of methanol. The suspension obtained was then applied to a paper support at a rate of 23 g. of lead(II) iodide/sq. m. After drying, this material was dipped in a 2% solution of potassium metaarsenite (KAsO_2) in methanol, and when still wet exposed image-wise for 60 sec. by means of a Philips HP 80 lamp. A black image on a yellow background was obtained.

EXAMPLE 20

Example 19 was repeated with the difference, however, that the solution of potassium metaarsenite was replaced by a solution of $(\text{H}_3\text{C})_3\text{C}-\text{NH}_2 \cdot \text{BH}_3$. A black image was obtained.

EXAMPLE 21

3 g. of poly(vinyl-n-butyral) and 5 g. of lead(II) bromide were ball-milled for 12 h. in 47 g. of methanol. To the suspension obtained a solution was added of 2 g. of 1-ascorbic acid in 23 g. of methanol. This suspension was applied to a paper support at a rate of 4 g. of lead (II) bromide/sq. m. After drying, the material was exposed through a transparent negative in a Buroza 600 (trade name) apparatus at a speed of 2 cm./sec. The exposed material showing only a faint image was then successively dipped in the following bath:

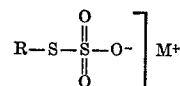
- (a) 10 sec. in a 5% solution of copper (II) chloride-2-water in demineralized water
 (b) 20 sec. in a 5% solution of sodium dithionite in demineralized water
 (c) 10 sec. in running water.

After drying a dark grey copper image on a yellowish-white background was obtained.

We claim:

1. A print-out process for recording information comprising the step of information-wise exposing to active radiation a photosensitive recording material comprising a layer incorporating a photosensitive lead halide salt dispersed in an organophilic binder in a ratio by weight of 1/9 to 3/1 of salt to binder, the amount of said salt being at least 1 g./sq.m. of layer area, said exposure being for a time sufficient to produce in said photosensitive layer a visible image, said lead salt being sensitized with (1) a compound of the group consisting of:

- (1) thiol compounds or thiolates,
 (2) compounds corresponding to the following structural formula:



wherein:

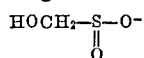
M^+ represents a cation and may be absent when the radical R already contains a cationic residue, and

R represents an alkyl, aryl or heterocyclic group,

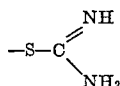
- (3) compounds yielding HSO_3^- ions,

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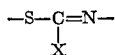
- (4) compounds yielding SO_3^- ions,
 (5) compounds yielding



- M—O—S—O⁻ ions, wherein M is a cation, or SO_2^- ions,
 (6) compounds yielding R— SO_2 —S⁻ ions, R.CO.S⁻, R.CS.S⁻ or R.CH.O⁻ ions, wherein R is an alkyl group, or an aryl group,
 (7) compounds yielding S⁻ ions or M—S⁻ ions, wherein M is a cation,
 (8) compounds yielding S_2O_4^- ions,
 (9) compounds yielding SCN^- ions,
 (10) organic isothiocyanates,
 (11) compounds containing a



- group,
 (12) compounds containing a —P=S group,
 (13) compounds containing a —S—S— group,
 (14) compounds containing a —S_x— group, wherein $x > 2$,
 (15) compounds containing a homopolarly bound —S—R₁ group, wherein R₁ is an acyl, alkyl, aryl, or heterocyclic group, linked through a carbon atom to the sulphur atom,
 (16) compounds containing a



- group, wherein X is an amino or hydrazino group and said sulphur-containing group makes part of a heterocyclic ring or ring system,
 (17) compounds of As, Sb or Sn, known as thiosalts,
 (18) compounds containing a >C=S group,
 (19) compounds yielding S_2O_3^- ions,
 (20) xanthates, i.e., salts of xanthic acid having the general formula $\text{R}_2\text{O.CS.SM}$, wherein M is a cation and R₂ is an alkyl radical, or
 (2) a compound described in Table 2 of the specification.
 2. The process of claim 1 wherein said lead salt is lead bromide.
 3. A photosensitive article according to claim 1, wherein the sensitizing agent is used in a ratio by weight comprised between 1:100 to 1:1 in respect of the lead compound.
 4. A process for recording information according to claim 1, wherein the photosensitive lead salt is lead iodide or lead bromide, or a crystalline mixture thereof.

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5. A process for recording information according to claim 1, wherein the organophilic binding agent is soluble in a lower alcohol.
 6. A process for recording information according to claim 1, wherein the organophilic binding agent is selected from the group consisting of sucrose benzoate, poly(vinyl-n-butylal), ethylcellulose, shellac, polyvinyl stearate, copoly(vinyl acetate/N-vinylpyrrolidone) and copoly(methacrylic acid/methyl methacrylate).
 7. A process according to claim 4, wherein said binder agent is water-permeable and the print-out image of the exposed photosensitive recording material is intensified by treatment with a physical developer.
 8. A process according to claim 7, wherein the treatment is carried out by means of a solution containing a reducing agent and metal ions of a metal that is more electropositive than lead.
 9. A process according to claim 7, wherein the recording material after its exposure is first treated with a solution containing metal ions of a metal that is more electropositive than lead and further treated with a solution containing a reducing agent.
 10. A process according to claim 8 wherein the said ions are silver ions, mercury(II) ions, mercury(I) ions, copper(II) ions or copper(I) ions.
 11. A process according to claim 1, wherein the recording material is exposed to active radiation in a wet state.

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